Handbook of Nonferrous Metallurgy

RECOVERY OF THE METALS

PREPARED BY A STAFF OF SPECIALISTS

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PREFACE OF THE FIRST EDITION

There are certain processes and materials that are common to all metallurgical operations: the use of refractories, of fuels, general methods of concentration, of filtration, etc. It has been my attempt to pick out these metallurgical common factors and to give each of them treatment in a separate chapter, following these chapters with others describing the metallurgy of each metal; or, in some cases, two or more metals, when there is no basic difference in their metallurgy, are treated in one chapter.

The scheme of treatment in the various chapters is not uniform—it intentionally is not so. In general the attempt is made to treat at greatest length those metals of prime commercial importance, but this plan is departed from if it is felt that existing literature on a certain metal is not readily accessible to the ordinary metallurgical engineer. While with copper, lead and similar metals, the subject matter of the chapter is the extraction of the metal from the ore, in the case of such metals as magnesium and aluminum, where it is extremely unlikely that the average engineer will ever be called upon to design a reduction works, or to work in any plant except one with an established metallurgy, much of the space is given to the useful alloys of the metal and how to work with them. In some cases analytical methods are given when it is felt that existing literature is deficient.

There is much that is elementary. The book is designed for the student as well as for the engineer and consultant, yet it is hoped that there is enough advanced material to make the book useful to the metallurgist of experience, particularly if he is confronted with problems somewhat outside his own specialty. There is no attempt to give extensive tables of basic data—for these the seeker is referred to International Critical Tables, the tables of the International Congress of Applied Chemistry, or to Landolt, or to the editor's "Metallurgists' and Chemists' Handbook."

To the contributors is due more than their signed work indicates, as there has been much cooperative correction and criticism. I must, however, acknowledge special indebtedness to Percy E. Barbour, who took over all work on the book during my various absences from the United States during the period of its preparation, and also to H. A. Megraw and Dr. Colin G. Fink, who have given liberally of their time, and to Thomas A. Wright, of Lucius Pitkin & Co., for his hints regarding rare-metal recovery.

Donald M. Liddell.

May, 1926.

CONTENTS

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CHAPTER I

METALLURGY OF ALUMINUM AND ALUMINUM ALLOYS

By Robert J. Anderson,[1] B. Sc. Met. E., D. Sc.

Introductory.—Aluminum is one of the lightest of the metals that are used in large quantities, having a specific gravity of 2.70 ±; once obtained as pig by modern reduction processes, it can be cast, worked, alloyed, and fabricated with moderate ease; metallurgically, it is one of the most interesting metals, but not one-tenth so much scientific investigation has been given to it as to iron. The merits of aluminum and aluminum alloys have been forced upon the engineering trades against a not inconsiderable opposition, and their worth as engineering materials has been proved beyond any doubt. Aluminum has established a place for itself among the nonferrous metals because of its intrinsic worth and, particularly, through its applicability to aircraft construction. Although aluminum is one of the most abundant metals of the earth's crust, it is at the same time one of the newest metals that have attained commercial importance.

Historical Survey.—Aluminum, as a metal, cannot lay claim to great antiquity, as contrasted with iron, copper, and the copper alloys, and it was a rare metal as late as 1850. Civilization is indebted to H. Sainte-Claire Deville for the pioneer work on reduction processes for the manufacture of metallic aluminum, but other investigators had carried out work prior to the eminent French chemist. Aluminum was first isolated by Oersted in 1825, who reduced aluminum chloride with potassium amalgam. The discovery of the metal has often been credited to Wöhler, who in 1827 reduced the chloride with potassium. Up to 1845, Wöhler had been able to produce only small amounts of aluminum, but still the amounts were sufficient to determine most of its properties. The attempts of early investigators to produce aluminum are described at length in some of the older texts (cf. Richards[2], Minet[3], *et al.*).[2]

To H. Sainte-Claire Deville belongs the honor of having isolated aluminum in fairly large amounts in 1854. Deville first made aluminum by the reduction of aluminum chloride with potassium, and later improved the process, substituting the

[1] This chapter has been revised by the editor, 1944.

[2] Throughout this chapter reference numbers apply to the appended bibliography, except in the case of obvious footnotes.

cheaper sodium for potassium. Deville also perfected processes for the manufacture of sodium, which greatly reduced the price of both sodium and aluminum. The Deville processes, however, were all expensive and not adapted to the cheap production of aluminum in large tonnages. Aluminum was made in small amounts in France and England by the Deville-Castner sodium-reduction method until the invention of the Hall-Héroult process in 1886–1887, which drove all other processes from the field. In 1886, the Cowles process[12] calling for the reduction of alumina by carbon in the presence of a metal (*e.g.*, copper) in the electric furnace, was patented and used commercially. This was the first successful thermal process, but it yielded aluminum alloys and not aluminum.

In 1886, Hall in America and Héroult in Europe found independently that alumina dissolved in a liquid bath of aluminum fluoride and the fluoride of another metal yielded an electrolyte that would be decomposed by the electric current according to

$$Al_2O_3 = 2Al + 3O$$

The effect of the Hall-Héroult electrometallurgical method on the price of aluminum was felt soon after 1886, and all other processes were driven from the field by 1892. In 1855, the price of aluminum was $113 per pound, in 1890 it was $2.38, in 1900 it was 23 cents, and in 1920 the lowest price, 16½ cents, was reached, until the present war. In the interim from 1920 to 1939, the price varied from 20 to 33 cents.

Many workers have been associated with the rise of the aluminum industry. In addition to those mentioned above may be mentioned the names of Davy, Bunsen, the Tissier brothers, Webster, Grätzel, Kleiner, Moissan, Ruff, Guilini, Askenasy, Bradley, Winteler, Serpek, Doremus, Krause, Grabau, Frishmuth, Netto, Welden, and Richards.

Producers and Output.—The aluminum industry of the world has grown by leaps and bounds since the metal became relatively cheap commercially. In tonnage, aluminum now stands second among the nonferrous metals, and it is exceeded only by copper. The optimistic forecast that Dr. J. W. Richards made in the early years of this century, that the production of aluminum would overtake that of lead by 1930 and zinc by 1940, was not fulfilled, but it is interesting to note that in 1943 with a production of 1,840,358,000 lb. in the United States it passed both of these nonferrous metals.

Aluminum Ores and Bauxite Mining.—Aluminum is the most abundant of the commercial metals and is third in abundance of the elements in the earth's crust, following oxygen and silicon. Aluminum is nearly twice as abundant as iron, and constitutes about 7.85 per cent of the earth's crust (Clarke). Aluminum is an essential constituent of all important rocks, except the sandstones and limestones, but even in these its compounds are common impurities. Aluminum never occurs native, and, except for its fluorides, it invariably occurs as oxidized compounds. Thus, it is found mainly in the silicates, such as the clays, micas, and feldspars; as the oxide, corundum; as the hydroxide, bauxite; as the fluoride, in cryolite; and also in various phosphates and sulphates. Although aluminum minerals occur widely, few of these can be employed as ores in the manufacture of aluminum. Bauxite is the base ore for aluminum reduction and bears the same relation to aluminum that hematite does to iron. Cryolite, either natural or artificial, is the basis of the reduction-cell bath. The utilization of other materials will be discussed later in this chapter.

Bauxite and Related Minerals.—Theoretical bauxite has been given the formula $Al_2O_3.2H_2O$, but the usual ore has a chemical composition midway between diaspore, $Al_2O_3.H_2O$, and gibbsite, $Al_2O_3.3H_2O$; sometimes it is near the one and sometimes near the other. Bauxite is an earthy mineral and never crystallized; it occurs in a variety of forms, but usually has a pisolitic or oölitic structure, with rounded concretionary

grains embedded in a claylike mass. The color ranges from light cream through various shades of brown to a deep brownish red, depending on the iron content. Bauxite takes its name from the village of Les Baux, near Arles in France, where it was first found by Berthier. The following physical properties of bauxite may be noted as an aid to identifying the mineral: hardness, 1 to 3 (Mohs' scale); specific gravity, 2.55; melting point—on heating it changes to Al_2O_3, which, when pure, melts at 1880 to 2050°C.; index of refraction, 1.57; color, white, cream, yellow, brown, gray,

FIG. 1.—Microstructure of bauxite pisolite with oölitic matrix; ×11. (*Shearer.*)

or red; streak, variable; luster, dull to earthy; cleavage, irregular fracture; transparency opaque; tenacity, crumbly. Diaspore and gibbsite are associated with bauxite and found under the same conditions. Laterite is an aluminous ore, which is essentially a mixture of iron hydrate, aluminum hydrate, and silica in varying proportions. The Indian aluminum ores are laterites. Figure 1 shows the microstructure of a hard, high-grade, pisolitic bauxite from Georgia.

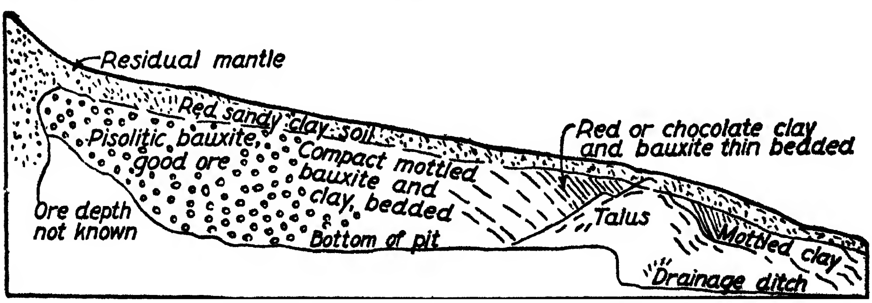

FIG. 2.—Typical bauxite deposit. (*Hayes.*)

Various theories have been advanced by geologists to account for the deposition of bauxite in the earth's crust. Bauxite occurs under a variety of conditions that suggest dissimilarity of origin, and no one theory appears to account for all cases. Figure 2 shows a section of a typical bauxite deposit. The theory of deposition has been discussed by Hayes[15] among others.

Commercial Bauxites.—Bauxite occurs at a number of places in the world, but high-grade deposits are not numerous, and it appears that known bauxite reserves

have a lower ratio to annual use than have the ores of any other common metal. Commercial bauxite ore is a hydrated oxide of aluminum, or a mixture composed of at least two and probably three hydrates, mixed with various impurities, chiefly iron oxide, silica, clay, and titania. Other impurities present are calcium oxide, magnesia, potassium oxide, and sodium oxide, in subordinate amount. The water content, both mechanical and combined, is variable over a wide range. Table 1 gives the chemical composition of some bauxites from various sources, which will serve to indicate the range of a variety of deposits. The color of bauxites varies considerably depending upon the iron-oxide content, being whitish when silica is predominant and red when

TABLE 1.—ANALYSES OF SOME BAUXITES FROM VARIOUS SOURCES[1]

Source	Chemical composition, constituents per cent						
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	Loss on ignition	Other constituents	Total
United States:							
Arkansas[a]	10.0	4.0	52.0	4.0	30.0	....	100.00
Arkansas[a]	4.0	4.0	53.0	10.0	29.0	....	100.00
Alabama[a]	2.10	3.12	61.0	2.20	31.58	....	100.00
Alabama	21.08	2.52	48.92	2.19	23.86	P_2O_5, trace	98.57
Georgia	6.62	1.05	64.91	0.28	33.53	....	100.39
Georgia	9.08	3.44	57.28	0.96	29.12	....	99.88
Austria:							
Sonnthal	6.32	0.91	64.05	15.93	13.28	....	100.49
Feistritz	13.60	....	57.25	0.97	24.38	CaO, 1.80; P_2O_5, 1.40	99.40
Croatia:							
Rudopolje	6.30	....	66.02	14.82	12.70	....	99.84
Grgienbrieg	10.29	....	50.61	26.89	11.29	....	99.08
Dalmatia:							
Moséc	0.87	....	59.27	24.36	15.93	....	100.43
Ilvar	30.47	....	29.05	16.24	17.14	CaO, 6.79; MgO, trace	99.69
France:							
Var	0.30	3.40	69.30	12.90	14.10	....	100.00
Bouches-du-Rhône	4.80	3.20	55.40	24.80	11.60	....	100.00
Germany:							
Garbenteich	1.10	3.20	50.92	15.70	28.60	CaO, 0.80; MgO, 0.16	100.58
Firnewald	4.92	2.80	53.10	10.62	27.80	CaO, 2.62; MgO, trace	99.86
Hungary:							
Bihárhegység	6.69	3.10	58.70	19.23	11.80	CaO, 0.80	100.32
Királyerdö	1.62	1.15	60.83	25.82	11.31	....	100.73
Ireland							
Antrim	6.01	....	61.89	1.96	27.82	....	97.98
Antrim	15.05	....	43.44	2.11	35.70	....	96.30

[a] Approximate composition.
[1] From different published analyses.

iron oxide is present in important amount. In a general way, the range of composition of bauxites is as follows: alumina, 55 to 65; silica, 5 to 30; ferric oxide, 1 to 25; and loss on ignition, 12 to 40 per cent. About 3 per cent of titania is associated with these oxides, and this is characteristic. Bauxites may be roughly classified, on the basis of their impurities, as follows: (1) high in iron and low in silica (red varieties); (2) low in iron and high in silica (white and gray); and (3) iron and silica contents about the same, either high or low. Bauxite is graded according to chemical composition and sold to the consuming industries on the basis of chemical analysis. The grading and the marketing of bauxite have been discussed by Hill[31] and Ladoo[44].

Bauxites are used for abrasives, for chemical and refractory manufacture, and for the preparation of high-alumina cements, as well as for aluminum reduction; the grade of ore required is variable, depending upon the use. For different uses, the grades of bauxite desired in American practice are as follows:

For aluminum manufacture: alumina, Al_2O_3, more than 52 per cent; silica, SiO_2, less than 4.5 per cent; and ferric oxide, Fe_2O_3, less than 6.5 per cent. (At the present time, bauxite, carrying less than 50 per cent Al_2O_3 and up to 15 per cent SiO_2, is being used.) High-grade bauxites for aluminum manufacture sometimes contain 58 to 65 per cent Al_2O_3, as little as 1 per cent Fe_2O_3, and 3 to 5 per cent SiO_2.

For chemical purposes (alum and aluminum sulphate preparation): alumina, Al_2O_3, more than 52 per cent; low ferric oxide and titania are preferable, *e.g.*, less than 3 per cent of each, but for some uses less pure ores are employed; requirements on silica are not set, but bauxites containing up to 19 per cent SiO_2 are used. It is definitely required that the alumina shall go readily into solution in dilute sulphuric acid.

For abrasives: various grades of bauxite are employed, but those low in iron and titanium are preferred. Generally, the requirements are: less than 5 per cent SiO_2, preferably 3 per cent; 2½ to 4 per cent TiO_2; and 3 to 5 per cent Fe_2O_3.

For refractories: the principal requirement is low iron and titanium contents, but the silica may be fairly high. So-called high-alumina clays, containing 48 to 52 per cent Al_2O_3, and high-grade diaspore, containing up to 80 per cent Al_2O_3, are now used in the refractory industry.

Cryolite.—Cryolite is an aluminum mineral of the composition Na_3AlF_6 (or $3NaF.AlF_3$), required in the production of aluminum, being the chief constituent of the electrolytic bath and used to dissolve the alumina. The actual composition of pure cryolite is 32.8 per cent sodium, 12.8 per cent aluminum, and 54.4 per cent fluorine. The only commercial source of cryolite is the deposit at Ivigtut, Araukfiord, South Greenland, owned by the Kryolith Mine & Handelsselskabet, A/S, of Copenhagen, Denmark. The high price of cryolite has led to the production of artificial cryolite, and this is now used generally in aluminum manufacture. Methods of preparation for artificial cryolite are described by Pattison[4], Mortimer[8], and others. In the Howard process,[1] the artificial product is prepared by the interaction of aluminum fluoride and sodium nitrate in the presence of ammonium fluoride, according to

$$Al_2F_2 + 6NH_4F + 6NaNO_3 = Al_2F_4.6NaF + 6NH_4NO_3$$

In the Hulin process, pure hydrated alumina is treated with hydrofluoric acid, and the resulting product is saturated with sodium dioxide, giving artificial cryolite. Doremus also leached aluminous material with hydrofluoric acid.

Other Aluminum Minerals.—A few other aluminum minerals may be mentioned. Alunite, $K_2O.3Al_2O_3.4SO_3.6H_2O$, is a hydrous sulphate of aluminum and potassium, found in many places, and worked at Tolfa, Italy, and in Utah and Colorado. Alunite has been studied considerably as a source of both alumina and potash. Corundum is the sesquioxide of aluminum (Al_2O_3). It does not occur in sufficiently large deposits to make it an ore, but it was formerly used in the Cowles process for manufacturing aluminum alloys. The feldspars are an important group of rock-forming minerals containing aluminum, and some experimental work is being done on them as sources of alumina. The feldspars vary widely in composition and include such minerals as orthoclase, $KAlSi_3O_4$, and anorthite, $CaAl_2Si_2O_4$. Labradorite, a feldspar, found in large quantities in Norway, has been used experimentally as a source of alumina for aluminum manufacture. Leucite, potassium-aluminum

[1] U. S. patents, 1511560 and 1511561, Oct. 14, 1924.

metasilicate, $KAl(SiO_3)_2$, has been employed as a source of both alumina and potash. The well-known china clay, kaolinite, is a basic orthosilicate of aluminum, corresponding to $H_4Al_2Si_2O_9$, and is one of the most important minerals of aluminum. The mineral kaolin is known variously as white china clay, pure white clay, and fuller's earth. The great purity of high-grade kaolin and the large available deposits stamp it as the logical ore for the manufacture of aluminum, but it cannot be now employed because of the cost of separating the alumina from the silica. Common clays are simply very impure kaolins. Sillimanite, cyanite, and andalusite are three aluminum minerals of great importance to the ceramic industry because of their conversion on firing to a compound known as mullite or artificial sillimanite, which latter possesses very useful properties. The formula for sillimanite, cyanite, and andalusite is $Al_2O_3.SiO_2$. There are many other aluminum-bearing minerals, including some of our prized gems.

Bauxite Mining and Preparation.—Bauxite is mined ordinarily by open-pit methods, since the producing bodies are near the surface. Ladoo[44] has discussed the mining operations of the American Bauxite Co., in Arkansas, which are typical of large-scale production. The ore bed at Bauxite, Saline County, runs about 11 ft. thick, and the overburden is 25 to 140 ft. thick. In mining, the overburden is first stripped off by steam shovel, and the stripped surface is then cleaned and swept. The ore is loosely consolidated, but it is usually too hard to be mined without blasting. Low-strength dynamite is used for blasting. The loosened ore is loaded by steam shovel on cars. In the Georgia-Alabama-Tennessee district, the ore occurs in lenticular and irregular deposits which do not lend themselves to steam-shovel operation, and all mining is done by hand.

It should be pointed out that the concentration or beneficiation of loosely consolidated bauxite mixed with clay has been tried at a few mines in the United States, using log washers, but this practice is now rare here. In Germany, ores from many small concessions in Hesse were washed at a central washing plant. Recently, considerable interest has been displayed in the possibility of beneficiation of low-grade bauxites and bauxitic clays because of the dwindling of high-grade bauxite. Everhart has shown that clay can be separated from bauxite by washing in the presence of small amounts of added peptizers, *e.g.*, sodium hydroxide and the more strongly adsorbed sodium salts.

Bauxite, when mined, may be given preliminary treatment on the ground, depending on the nature of the ore. The bauxites found in the United States ordinarily contain 15 to 33 per cent combined water, together with a varying amount of mechanically held moisture, and, since the ores must ordinarily be shipped long distances, it is usual to dry the ore at the mines so as to save freight and to facilitate fine grinding for later use. For the preparation of alumina to be used in the manufacture of aluminum, bauxite is ordinarily crushed and dried at the mine, but not ground finely. In crushing, the crude ore is run through gyratory or other types of rock breakers and crushed to small nut size. Gyratory breakers are generally used for hard ores and disintegrators for soft ores. It is desirable to calcine most bauxites in order to remove organic matter which would interfere with the precipitation of aluminum hydroxide in the preparation of alumina, to oxidize ferrous oxide to ferric oxide, and to remove water which may be present in sufficient amount to form a pasty mass and clog the screens in fine grinding. For calcination, the ore may be heated at about 600°C. in cylindrical rotary kilns of the type shown in Fig. 3. By such treatment, the moisture content is reduced to ½ to 1 per cent. Kilns for calcination are 3 to 7 ft. in diameter and 30 to 100 ft. long.

The Bureau of Mines[78] has carried out some experiments on the flotation of bauxite. In its work it was found profitable to use either gravity or magnetic con-

centration for the removal of iron and titanium minerals, followed by flotation for the recovery of hydrated aluminum oxides and the rejection of the silica. To obtain a satisfactory separation between the hydrated aluminum oxides and the kaolinite, it is necessary to avoid floccules of finely divided bauxite and clay. Sodium hydroxide is the preferred dispersant. A pulp of 10 to 15 per cent solids gave the most satisfactory results. The most effective collectors for the hydrated aluminum oxides are oleic acid and fish-liver-oil fatty acid. The fatty resinous by-products of the paper-mill waste liquor are also fairly effective collectors, but they are more pronounced frothers. It would appear that if the bauxite were not crystaline in character there would be a heavy reagent loss, but the paper referred to does not touch on this phase of the process.

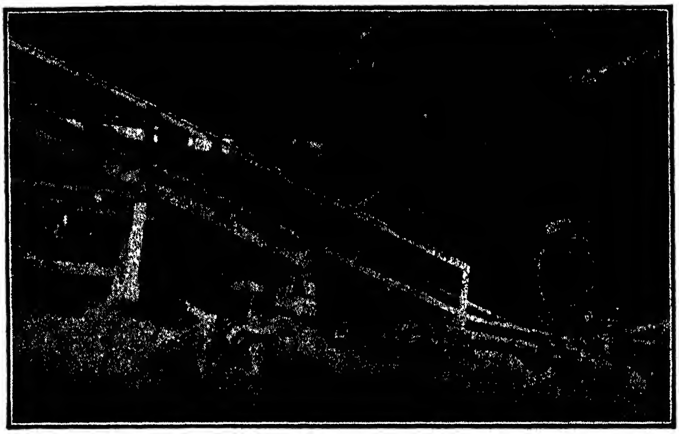

FIG. 3.—Rotary calcining kilns.

Production of Aluminum.—For the past fifty-five years, the production of metallic aluminum on a commercial scale has been carried out in two essential steps: (1) the preparation of alumina of high purity from bauxite, and (2) the electrolysis of the alumina in a liquid bath of cryolite plus other added salts. The reduction of alumina, Al_2O_3, to aluminum cannot be done by carbon smelting, as with iron, copper, lead, and other commercial metals. Or, more precisely, alumina can actually be reduced by carbon, but, at the temperature and conditions of such reduction, the aluminum so reduced either volatilizes, oxidizes, or interacts with carbon monoxide or dioxide, forming aluminum carbide or aluminum oxide. Modern processes for aluminum reduction depend primarily on the preparation of substantially pure alumina, and this is the first step in the treatment of bauxite after calcination and grinding.

As pointed out previously, crude bauxite contains varying amounts of ferric oxide, silica, titania, and other impurities; these oxides must not be present in the alumina which is added to the electrolytic bath, otherwise the reduced metals, iron, silicon, etc., will appear in the resultant aluminum. It should be emphasized that one of the chief difficulties in the metallurgy of aluminum lies in the fact that the metal, after being produced, cannot be readily refined, as can copper and others of the commercial metals, and the purity of the metal secured by electrolytic dissociation depends primarily upon the purity of the alumina and the electrolytic bath. Many patents have been issued which apparently cover every conceivable method for obtaining aluminum from aluminum-bearing minerals, but the only commercial process is that one calling for the electrolytic dissociation of alumina dissolved in a liquid bath of cryolite plus other added salts. Electrolytic methods for the dissociation of

aluminum compounds are not applicable in aqueous solution, and fused electrolytes must be employed. For the electrolytic process, a primary requisite for commercial practice is a source of cheap electric current, since an enormous amount of current is required, and most of the aluminum-reduction plants in the world, except certain ones in Germany, consume electric energy derived from hydroelectric plants. For this reason, aluminum-reduction plants are normally situated within easy access of waterfalls, and steam-raised electric power is rare as a source of current for economical aluminum production.

Preparation of Alumina.—In the present Hall-Héroult process, the raw materials for the production of aluminum include substantially pure alumina, cryolite (plus calcium and aluminum fluorides for the bath), and carbon electrodes, and the first step in the manufacture of the metal consists in the purification of bauxite by chemical methods, whereby substantially pure alumina is produced. There are two main processes for the preparation of alumina, although many patents have been taken out for doing this in one way or another. These processes are (1) the Bayer process, and (2) the Deville-Pechiney process. The preparation of alumina has been discussed at length in the literature [2, 4, 8, 11, 30].

The usual process employed for the preparation of alumina from bauxite is the Bayer process, a wet chemical method. In this, the chemical principle involved is the formation of sodium aluminate by the treatment of bauxite with aqueous sodium hydroxide and the subsequent precipitation of aluminum hydroxide from the sodium aluminate, followed by calcination of the aluminum hydroxide to alumina, Al_2O_3. In practice, calcined bauxite is first ground, *e.g.*, in a ball mill, to 100 mesh or finer, and this is next mixed with aqueous sodium hydroxide, specific gravity 1.45 (44.8°Bé.), in a vessel fitted with stirrers. After intimate stirring, the mixture is then run into steam-jacketed autoclaves and digested for 2 to 8 hr. under 50 to 70 lb. pressure at 150 to 160°C. The alumina of the bauxite is acted upon by the sodium hydroxide with the formation of sodium aluminate, according to

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$$

The impurities ferric oxide and titania are unaffected by the sodium hydroxide, as is the greater part of the silica. Part of the silica is dissolved and reacts with alumina and sodium oxide to form insoluble double aluminum sodium silicate. Dissolution of silica is prevented by adding lime to the bauxite during fine grinding, which forms insoluble calcium silicate and prevents loss of alumina. About 90 per cent of the alumina in the bauxite is dissolved by the digesting treatment.

When the digesting treatment is completed, the liquor (including the residue of impurities) from the autoclaves is blown into large iron settling tanks of about 1600 cu. ft. capacity and allowed to settle for 4 to 5 hr. so as to effect separation of the solid impurities. The settled residue contains ferric oxide, silica, titania, and other impurities from the bauxite, as well as some alumina not dissolved, and is known as "red mud." This was formerly discarded, but some of it is now being reworked by the lime-soda sintering process, as a source of further alumina, and for titanium. The sodium aluminate liquor from the autoclaves is first diluted from specific gravity 1.45 to 1.23 (26.9°Bé.), and after settling in the tanks is run through filter presses for removing suspended matter and into large precipitation tanks or decomposing vessels. Figure 4 shows a type of tank fitted with stirring apparatus used by European producers[44] for precipitation of aluminum hydroxide. In precipitating aluminum hydroxide from the sodium-aluminate liquor, a small amount of freshly prepared aluminum hydroxide is added to the tank and the whole is stirred (the so-called "seeding" operation); aluminum hydroxide is precipitated from the liquor over a period of time running up to about 60 hr. About 70 per cent is precipitated in 36 hr.,

and the remainder precipitates on further standing. The precipitated aluminum hydroxide settles to the bottom of the tank, where it is drawn off and put through filter presses, yielding a product for calcination to alumina. The sodium-hydroxide liquor from the tanks is evaporated in vacuum pans and concentrated to specific gravity 1.45 for re-use in the treatment of raw bauxite.

After filter pressing, the partially dried aluminum hydroxide is calcined so as to drive off water and yield substantially pure alumina. This calcination is generally carried out in tubular rotary kilns, lined with firebrick, and similar to those used in calcining bauxite or burning cement. The kilns are run at 1000 to 1100°C. The resulting alumina contains 98 to 99.5 per cent Al_2O_3, and may contain up to 0.30 per cent mechanical water, 0.50 per cent combined water, 0.20 per cent silica, 0.10 per cent ferric oxide, and other impurities in subordinate amounts. After calcination, the alumina is ready for use in the electrolytic-reduction cell.

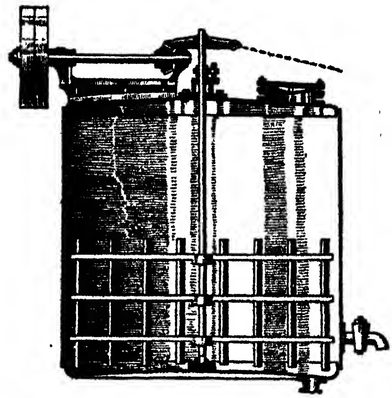

FIG. 4.—Bayer precipitation tank.

The Deville-Pechiney (or Le Châtelier-Morin) process was formerly the principal process for the preparation of alumina, but this has been largely supplanted by the Bayer process. The former is still used, however, for the treatment of bauxites especially high in iron and forms the basis of the so-called lime-soda sintering process for impure ores. In the original process, ground bauxite, after calcination, is mixed with sodium carbonate, about 1 to 3 parts sodium carbonate and 1 part bauxite, and the mixture is roasted in a rotary or reverberatory furnace for 2 to 4 hr. at 1000 to 1100°C. A small amount of powdered coal is sometimes added to the mix. The sodium carbonate combines with the alumina, carbon dioxide is evolved, and the impurities are unattacked. The roasting must be done with care to avoid melting of the mix, and the product of the roast is a grayish-brown substance, consisting of a mixture of sodium aluminate and the impurities. The reaction is

$$Al_2O_3 + Na_2CO_3 = NaAlO_2 + CO_2 \uparrow$$

After roasting, the mass is lixiviated with hot water, whereby the sodium aluminate is dissolved, while the silica, ferric oxide, and titania, being insoluble, are left as a residue. The liquor is settled for the removal of the solid impurities, as in the Bayer process, and is then passed through filter presses, for removal of any suspended matter, and then into tall precipitation tanks. For precipitation, carbon dioxide is blown into the liquor, and the reaction is

$$2NaAlO_2 + CO_2 + 3H_2O = 2Al(OH)_3 + Na_2CO_3$$

This precipitation requires 4 to 5 hr. and is carried out at 70°C. The precipitated aluminum hydroxide is filter pressed, dried, and calcined, as in the Bayer process, yielding alumina[76].

Some other processes have been devised and actually employed for the preparation of alumina, and will be discussed below. Certain other methods for obtaining a compound of aluminum (such as the fluoride, nitride, carbide, and chloride) from aluminum minerals have been worked out. A few of these possess potentialities, but the majority of them have no discernible commercial possibilities. While many processes have been devised for the preparation of alumina from clays and other

fairly high aluminous minerals, none of these had been commercial in the United States, under peacetime conditions, though some had a limited use abroad. A few processes that have been employed commercially or have reached the semicommercial scale are discussed briefly below.

Treatment of Low-grade Bauxites.—Partly owing to the dislocation of steamship communications and partly owing to an actual shortage of high-grade bauxite, a great deal of attention has been given in the last few years to the recovery of alumina from second-rate materials. Probably in the United States the largest amount of alumina recovered from low-grade materials has been by the so-called "lime-soda-sinter process," sometimes known as the "Deville process." In this process, the material is mixed with limestone and soda ash and calcined; the sintered mass is then leached with hot water for the extraction of the soluble alumina; the solution is treated in an autoclave at a temperature of 160°C. and 85 lb. pressure, under which condition the bulk of the silica forms insoluble sodium-aluminum silicate. After settling and filtering, the solution is treated with carbon dioxide for about 5 hr. at 70°C., to precipitate the alumina[72].

A variation of this lime-soda-sinter process has been tried at the Monolith Portland Midwest Co. pilot plant at Laramie, Wyo. At this plant an anorthosite has been substituted for bauxite and treated by the lime-soda-sinter process. The results at the pilot plant were so encouraging that the WPB authorized the erection of a semi-commercial plant and indicated that the pilot plant would be used to test the lime-soda-sinter process on clays.

Ammonium Sulphate Exchange Process.—In the best known of these processes a mixture of pulverized clays and ammonium sulphate is treated at temperatures of 373 to 400°C. in a rotary kiln, ammonia being evolved and ammonium aluminum sulphate being formed[71]. The reacted mass is then leached at 95 to 100°C. with water slightly acidulated with sulphuric acid and the solution separated from the insoluble residue. The ammonium aluminum sulphate is recovered by crystallization and after being redissolved is treated with the ammonia and ammonium carbonate (the last resulting from the mixture of ammonia with the combustion gases of the initial treatment).

Aluminum hydroxide is precipitated and filtered off, and the ammonium sulphate is recovered by crystallization for re-use with more clay or low-grade bauxite. The basic patents so far as the editor knows are the German patents of Hess (376717 and 388996) and of Riedel (386614).

The Buchner process is a variation of the ammonium sulphate process and is sometimes known as the "Aloton process." In this, clay is heated with acid ammonium sulphate at 200°C. In other particulars the process is the same as that of the preceding paragraphs.

Another variation of the sulphate decomposition is the Peniakoff process in which clay or bauxite and sodium sulphate are heated together with a little coal at 1200 to 1400°C.

$$Al_2O_3 + Na_2SO_4 + C = 2NaAlO_2 + SO_2 + CO$$

Sulphuric Acid Process.—Practically all ammonium silicates can be decomposed with fair efficiency by sulphuric acid at temperatures in the neighborhood of 200°C. and with acids of about 1.25 specific gravity.

Sulphurous Acid Leaching.—This reagent has been experimented with for many years, the earliest patent on the subject being E. Raymond's U. S. patent 650763, taken out in 1902, and the latest known to the author being Goldschmidt's 2006851, taken out in 1935. The Goldschmidt process leaches with aqueous solutions of SO_2 under pressure at 60 to 80°C. Alumina and aluminum sulphite are precipitated on

release of pressure. The objections reported to the author are a tendency of iron to form soluble bisulphites and then to precipitate just as does the alumina, so that the precipitated alumina must be purified, and also the fact that the sulphur dioxide oxidizes to sulphur trioxide, resulting in a loss of the reagent.

Nitric Acid Process.—Nitric acid leaching has always been tried experimentally at temperatures in the neighborhood of 170°C. and 120 lb. pressure per square inch. The high cost of nitric acid and the loss of this reagent have prevented any commercial applications.

Hydrochloric Acid Leaching.—The best known of the hydrochloric acid processes is probably that of Chemische Fabrik Griesheim[73]. This is essentially a process to treat high-silica bauxites. The alumina and iron dissolve in hydrochloric acid, the solution being reduced after this treatment with sulphureted hydrogen. The solution is evaporated and heated to 300°C., which hydrolyzes the aluminum chloride in its own water of crystallization. If this temperature is not exceeded, the ferrous chloride is in the main water-soluble. However, it is reported that even with the most careful work, the alumina requires a cleanup with chlorine to free it from the last of the iron.

Dr. Arthur Hixson and Ralph Miller worked on a process for leaching roasted clay with concentrated hydrochloric acid[77], converting the aluminum and iron into soluble chlorides, but leaving the silica insoluble. The novelty in this process was the use of isopropyl ether to remove the ferric chloride from the solution. This could then be evaporated and the aluminum chloride hydrolyzed to give alumina and hydrochloric acid. The process required the circulation of one ton of isopropyl ether per ton of alumina recovered, and this was apparently the main reason for the National Academy of Sciences and the WPB refusing materials to give the process a trial. This need not be considered final proof that the process is unworkable.

Hydrofluoric Acid Leaching.—The use of hydrofluoric acid for leaching clays and low-grade bauxites has also been experimented with fairly extensively. The patents of Dr. Charles A. Doremus (723251 and 725683) are the oldest known to the author. Apparently the recovery of alumina was high, but there were heavy losses of the expensive reagent as insoluble fluosilicates and as silicon tetrafluoride.

Recovery from Alunite.—A number of processes have been used for the treatment of alunite, $K_2O.3Al_2O_3.4SO_3.6H_2O$; these were well summarized by Robert J. Anderson in the *Mining Magazine*, December, 1936, page 340. At the present time, a plant has been constructed near Salt Lake City to use the Kalunite process. The crude ore is crushed and given a dehydrating roast at 550°C., which renders it soluble in dilute sulphuric acid. The hot calcine is cooled to 200°C. and given a countercurrent agitation and leach in a solution of potassium sulphate and 10 per cent sulphuric acid. The countercurrent leach is operated to maintain an excess of roasted alunite in the first agitator so that the pregnant solution contains no free acid. This is an important step in eliminating impurities. The pregnant solution is filtered out and then cooled, normal potassium alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, crystallizing out. The alum crystals are washed, dissolved with dilute potassium sulphate solution, and treated in a continuous autoclave at a temperature of 200°C. The potassium alum is broken down into a basic alum, $K_2SO_4.3Al_2O_3.4SO_3.9H_2O$, plus sulphuric acid and potassium sulphate. The acid and potassium sulphate are recycled for the original leach, and the basic alum is calcined at 1000°C. to decompose it into alumina and potassium sulphate. The calcine is then leached with hot water to remove the soluble potassium sulphate, leaving behind the alumina. The leach solution is then evaporated to crystallize out potassium sulphate[69, 70].

The Moffat process is essentially the same except that the alum recovered in the process is broken down by a flash roast.

In Italy both alunite and leucite, $K_2O.Al_2O_3.4SiO_2$, have been used for the production of alumina and potash. The process used for the treatment of leucite is the Blanc process, which leaches with dilute sulphuric acid. It is reported that agitation cannot be used, as the silica gelatinizes when agitated and holds up much of the solution. It is claimed that if the leaching is done by straight percolation without agitation little trouble results from the silica.

Japan has probably produced much of its alumina by the following four methods and the Suzuki process described under Fusion Processes, below. In the Asada process, alunite is calcined at 600°C. and is treated with sulphuric acid and potassium sulphate. After filtering and cooling most of the aluminum salts out as alum. The mother liquor goes back to the solution cycle, and the potassium alum is decomposed into basic aluminum sulphate and acid potassium sulphate. (See page 11, discussion of Kalunite process, for details of further treatment.) In the Okazawa process (Showa potassium process), alunite, crushed and calcined at 600°C., is treated with potassium hydroxide. Potassium aluminate and sulphate go into solution, silica remaining behind. (See page 11, discussion of Kalunite process, for treatment of the sulphates.) In the Sumitomo process, alunite is leached with sulphuric acid. On cooling, alum and aluminum sulphate salt out and are filtered off, redissolved, and treated with ammonia, giving alumina as a precipitate and potassium and ammonium sulphates in solution. In the Tanaka process, alunite is calcined at 600°C., crushed, pulped with water, and treated with about 8 per cent its weight of ammonia. Potassium and ammonium sulphates are left in solution and are recovered for fertilizer use. The washed residue is treated with caustic soda (Bayer process). This is apparently the process sometimes described as the Showa sodium process.

Fusion Processes for Alumina Production.—Treatment of high-iron bauxite in the electric furnace has been practiced successfully on a commercial scale in Norway[71]. The Pederson process appears to be the one worked on by our own Bureau of Mines in a pilot plant to test the process. This should not be confused with the Pederson process that sinters clay with lime and subsequently leaches the melt with soda. This second Pederson process is of course a modification of the lime-soda-sinter process.

The Bureau of Mines reports that the only practical method of making calcium aluminate from high-silica bauxite is by a two-stage treatment. In the first stage, the silica and iron oxide are reduced to ferrosilicon. The molten slag from this operation, which contains 95 to 98 per cent alumina, is transferred to a second furnace where with the addition of lime monocalcium aluminate is produced. This compound is readily decomposed by sodium carbonate solution, producing a solution of sodium aluminate from which alumina can readily be recovered.

The Haglund process is also understood to have been in successful use in Scandinavia. In the original Haglund process, clay and pyrites were smelted, using a reducing agent to produce ferrosilicon and an aluminum sulphide slag, which was later hydrolyzed for the production of alumina. (Incidentally, this appears to be about the same as the old Halvorsen process.)

The later Haglund process reduced only about one-fifth of the alumina to aluminum sulphide. The mixture of aluminum sulphide and aluminum oxide gave a lower melting-point slag than that of the original process and also cut down the amount of ferrosilicon produced and marketed. In the newer process, as in the old, ferrosilicon was produced and formed a heavy layer under the slag. The slag was decomposed with water, and the sulphureted hydrogen that was generated was sold as such or was worked into sulphur for further use in the process.

The Suzuki process reduced clay with coke for the production of ferrosilicon, and the residual alumina was cleaned with chlorine at 500 to 600°C. A long discussion of this matter of purifying ferruginous alumina and bauxite was prepared by Dr. Colin G. Fink and V. S. de Marchi and published by the Electro-Chemical Society in its 1938

transactions, page 511. E. C. Eckel experimented at Mussel Shoals as early as 1934 on the treatment of low-grade bauxites carrying 30 per cent silica and 30 per cent iron sesquioxide[74]. From such a bauxite he produced ferrosilicon with a slag that carried less than 2 per cent silica and 1 per cent iron.

The Berger and Kuhne process smelted kaolin, clay, or bauxite with iron pyrites, magnesium chloride, and iron filings, aluminum chloride being distilled and condensed. The Miguet process fused clay, lime, and scrap iron with a reducing agent to produce ferrosilicon and calcium aluminate, but apparently these processes could not produce alumina in competition with the natural bauxite (see *U.S. Bureau of Mines Report of Investigations* 2393).

Loevenstein Process.—Of interest as an outstanding novelty is the process devised by Hirsch Loevenstein and operated on a pilot-plant scale in France by Jacques Fondal before the German invasion[77]. Clay is smelted in an electric furnace to a mixture of aluminum, silicon, iron, and impurities, and the product is treated in a bath of molten zinc. The aluminum only is soluble. The zinc is then distilled from the aluminum.

Serpek Process.—In the Serpek process, aluminum nitride is produced by heating ground bauxite and carbon in an atmosphere of nitrogen at 1600 to 1800°C. The aluminum nitride formed under these conditions can be decomposed with water.

$$AlN + 4H_2O = Al(OH)_3 + NH_4OH$$

The plant of the Southern Aluminium Co. was originally intended to use this process, but never worked commercially on it.

Primary Aluminum Manufacture.—The present commercial process for the production of aluminum is essentially the same as that described in the original Hall-Héroult patents of 1886 to 1888, and all aluminum made today is produced by the electrolytic dissociation of alumina dissolved in a bath of liquid (fused) cryolite plus other added salts. The sodium-reduction process need not be considered here, since it is only of historical interest, but it is important to direct attention to the Cowles alloy process. It should be pointed out that, although Hall applied for his patents in 1886, these were not granted until 1889, and in 1886 Héroult also applied for a United States patent on essentially the same process as described by Hall. The essential differences in the patent applications were in the composition of the electrolyte and the design of the furnace, but the two processes are identical to all intents and purposes. When the separate discoveries of Hall and Héroult were made simultaneously, there was no patent litigation, but the Hall company took the American field and the Héroult company the European field.

The Cowles process[12] for the manufacture of aluminum alloys direct from Al_2O_3 was patented by A. H. and E. H. Cowles[13] in 1885, and plants for conducting the process were built at Lockport, N. Y., and Stoke-on-Trent, England. In essence, the Cowles process called for the reduction of alumina by carbon in the presence of a metal (*e.g.*, copper) in the heat of the electric arc. While alumina can be reduced by carbon, as pointed out previously, the metal so reduced will either combine with the carbon, forming aluminum carbide; combine with carbon monoxide or dioxide, forming aluminum carbide or oxide; combine with any oxygen present; or else volatilize. In the presence of another metal, however, say copper or iron, the reduced aluminum alloys with the other metal, thereby forming an intermediate alloy. In the Cowles process, when copper is used, alloys containing 15 to 40 per cent aluminum and the remainder copper are produced, and these were diluted with copper in making aluminum bronze.

In the process, a correctly proportioned mixture of alumina, carbon, and copper is placed in an electric-arc furnace and smelted. Copper, or any other metal used for alloying, has no effect on the actual reaction, since what takes place is simple reduc-

tion of alumina by carbon at elevated temperatures, according to

$$Al_2O_3 + 3C = 2Al + 3CO$$

During the years 1885 to 1890, the alloys made by the Cowles process could be produced at a lower price per pound of contained aluminum than substantially pure aluminum itself, and as a consequence a considerable measure of success was had. The process is obsolete, but it may have had a war revival, to produce certain intermediate or light aluminum alloys by direct reduction from alumina.

Hall Aluminum Process.—In 1886, C. M. Hall, of Oberlin, Ohio, found[5] that alumina dissolved in a liquid (fused) solution of aluminum fluoride and another metal fluoride, *e.g.*, sodium, formed an electrolyte and that the alumina could be dissociated by the electric current, according to

$$Al_2O_3 = 2Al + 3O$$

The electrometallurgical principle involved in the process, then, is the electrolytic decomposition of alumina dissolved in a bath of fused fluorides of aluminum and other bases; the current causes dissociation of the alumina into aluminum and oxygen without appreciably affecting the solvent. This invention caused a revolution in the aluminum industry. It should be added that C. S. Bradley applied for a patent covering the electrolytic dissociation of aluminum compounds in 1883, but this patent was not granted[14] until 1892. This Bradley patent was the cause of litigation first between the Electric Smelting and Aluminum Co. (*i.e.*, the Cowles company) and Paul Héroult regarding title to it, and second between the Cowles company and the former Pittsburgh Reduction Co. (*i.e.*, the present Aluminum Co. of America). After long litigation it was decided by the courts that the Pittsburgh Reduction Co. in using the Hall patents had infringed the Bradley patent.

In development of the Hall process, it was found that cryolite made a good solvent for alumina, and cryolite, as such, or plus calcium and aluminum fluorides, is employed for the electrolytic bath in present practice. In the process, the aluminum is liberated and sinks to the cathode, while the oxygen goes to the anode, which it attacks, burning to carbon monoxide and finally to carbon dioxide on contact with the air. The electrolysis is carried out in a carbon-lined furnace or cell, the carbon lining serving as the cathode and separate carbon electrodes as the anodes. In the Hall reduction cell, the electric current serves two important functions, *viz.:* (1) it keeps the electrolytic bath liquid by the generation of heat, and (2) it causes electrolytic dissociation of the alumina. Theoretically, the decomposition voltage required is 2.8, but in practice about three times this is actually used.

As indicated, P. L. V. Héroult, of Paris, France, brought out a process in 1886 for the preparation of aluminum by the electrolysis of alumina dissolved in cryolite, and this process is identical in principle with that of Hall. Héroult's first patent[1] called for the preparation of aluminum and aluminum alloys by the electrolysis of alumina dissolved in cryolite, and in making aluminum alloys a negative electrode of the metal to be alloyed was employed. This method was never applied commercially to the production of alloys, but it was used for aluminum. In Héroult's[2] second method, a process for making aluminum alloys was specified, in which alumina was melted by the electric current and electrolyzed by the same current, using a liquid metal, *e.g.*, copper, beneath the aluminum as the cathode. The resulting product is an intermediate alloy of aluminum and copper, similar to that obtained by the Cowles process. Alumina, without copper or another metal present, cannot be electrolyzed to

[1] French patent 175711, Apr. 23, 1886.

[2] French 170003, Apr. 15, 1887; and U. S. patent 387876, Aug. 14, 1888; and other patents.

produce aluminum; since the metal would be volatilized at the temperature prevailing. This process was operated for a short time at Neuhausen, Switzerland, but was abandoned in 1891, and the production of aluminum taken up in accordance with Héroult's first patent.

Many methods have been devised for the production of aluminum both before and since the invention of the Hall-Héroult process, but all aluminum made now is produced by this process. The older methods have been discussed at length in the books by Richards[2] and Minet[3] and need not be considered here, but it is of interest to touch briefly upon some processes that have been devised in recent years. However, none of these is now commercial.

A method for the production of aluminum directly from aluminum-bearing minerals has been patented by Tone,[1] in which aluminum ore is smelted to aluminum carbide with carbon in an electric furnace, and this is then mixed with silica and smelted to an aluminum-silicon alloy or with aluminum oxide and smelted to aluminum. The process is uneconomic, even if it is technically sound. Betts[2] has patented a process entailing the smelting of kaolin in a blast furnace to an iron-aluminum-silicon alloy. This alloy is then oxidized, sulphurized, or chloridized to aluminum oxide, sulphide, or chloride, and in the sulphide the compound is electrolyzed to aluminum and sulphur. In a patent by Kissock,[3] an aluminum-silicate mineral is smelted with carbon to aluminum carbide, and this is converted to aluminum sulphide. The latter is electrolyzed in a suitable bath. Many carbon-smelting processes for the direct reduction of aluminum have been devised, but, as stated, these are all technically unsound. A number of patented processes call for the electrolysis of aluminum salts in aqueous solution, but these are unsound.

The fundamental principle of the Hall-Héroult process is the electrolytic dissociation of alumina dissolved in a bath of aluminum fluoride and the fluoride of one or more metals more electropositive than aluminum, *e.g.*, sodium, potassium, or calcium. The composition of the electrolytic bath is especially important, and this will be discussed briefly. Both natural and artificial cryolite are used as the base in making up baths, and the actual bath composition may vary over a fairly wide range. Cryolite melts at 995°C., and the eutectic mixture 81.5:18.5 cryolite-alumina melts at 935°C. By the addition of various salts, the melting point may be reduced to 700°C. The specific gravity of the liquid bath must be less than that of liquid aluminum at the operating temperature, since otherwise the dissociated metal would rise, instead of sink, and upset the cell. A typical bath contains 66.8 per cent aluminum fluoride and 33.2 per cent sodium fluoride. In the Hall process, the following composition has been employed for the bath: 59 per cent aluminum fluoride, 21 per cent sodium fluoride, and 20 per cent calcium fluoride. This bath dissolves 20 per cent alumina at the operating temperature. Cryolite has a specific gravity of 2.92 in the solid state and of 2.08 in the liquid state, while aluminum has a specific gravity of 2.70 in the solid state and 2.31 in the liquid state (at 900°C.). Hence at the operating temperature, the metal collects at the bottom of the bath.

The theoretical e.m.f. required for dissociation of the alumina in the process is 2.8 volts, but in practice at least three times this is necessary because of the resistance of the bath and connections and small losses here and there in the circuit. In general, irrespective of the type of furnace, each unit requires 6.5 to 7.5 volts for operation, and in starting, a wider range, 5.5 to 8.5 volts, is necessary. It is not economical to build dynamo-generators of such low voltage, and consequently 30 to 40 furnaces are connected in series; thus, the operating voltage for 35 furnaces would be 250 volts. The

[1] U. S. patent 961913, June 21, 1910.

[2] U. S. patent 938634, Nov. 2, 1909.

[3] U. S. patent 1052727, Feb. 11, 1913.

current density varies over a rather wide range, *e.g.*, 1.5 to 3 amp. per sq. cm. in certain French furnaces, and 650 to 750 amp. per sq. ft. in some American cells. The current employed depends upon the size and the number of electrodes—8000 to 10,000-amp. lines are common, and there are larger furnaces using 15,000 to 20,000 amp. Theoretically, there should be 0.33912 g. of aluminum produced per ampere-hour, or 0.7476 lb. per 1000 amp.-hr. The theoretical anode consumption is 0.67 lb. per pound of aluminum produced, but in practice this amounts to 0.8 to 1.0 lb. The consumption of alumina per pound of aluminum produced is about 2 lb. in practice—1.888 lb. theoretically—and about 0.1 lb. of cryolite or bath material is consumed.

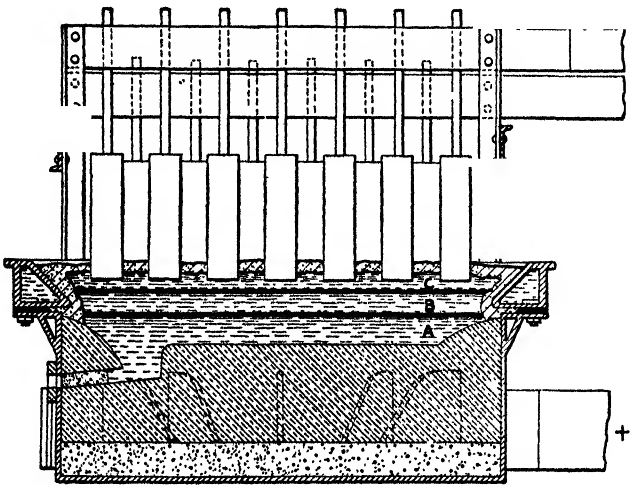

FIG. 5.—Hoopes refining cell.

About 12 kw.-hr. is required to produce 1 lb. of aluminum; hence a difference of 1 mill in the cost of power makes a difference of 1.2 cents per lb. in the cost of the aluminum.

As mentioned in a later paragraph (*cf.* Commercial Aluminum, below), the product of the Hall-Héroult reduction cell is not pure aluminum but contains appreciable amounts of impurities. Many attempts had been made to refine impure aluminum and to produce *pure* metal, but this had not been accomplished until the Hoopes process was developed. The method is described in patents[7] granted to Hoopes and others and owned by the Aluminum Co. of America. Detailed discussion of the process cannot be given here. Briefly, a cell is employed in which there are three horizontal layers; the lowest layer is a liquid aluminum-copper alloy anode, above this is a layer of fused cryolite-barium fluoride solution (the bath electrolyte), and floating on top is the cathode of pure liquid aluminum. The cell operates at about 6 volts and 20,000 amp. Cathode metal containing as high as 99.98 per cent Al has been produced in the Hoopes cell in regular operation. The mechanical, physical, and chemical properties of *pure* aluminum are markedly different from those of the ordinary 99+ per cent commercial metal, but the mechanical properties are inferior to the many carefully prepared alloys.

Aluminum-reduction Furnaces.—All furnaces now in use for the electrolytic production of aluminum, other than the Hoopes cell, are essentially the same in general design, although they vary considerably in constructional detail. The usual furnace consists of a rectangular box of mild steel lined with a refractory material of low thermal and electrical conductivity, and within this a heavier lining of rammed

carbon forming the cathode. This carbon lining is made of petroleum coke with a suitable oil or tar binder rammed in place; plates of iron may be molded in the bottom to form the cathode connection. In some furnaces, the lining is made as a separate unit, which is molded and baked similar to the anodes. There is great advantage in this type of lining, since a furnace that becomes inoperative can be renewed with a minimum of labor by simply removing the old lining and replacing it with a new unit. Figure 6 shows the general lines of the modern Hall-Héroult furnace with the anodes. In some furnaces, electrodes of carbon are embedded in the bottom of the furnace.

In all types of furnaces, the bottom is inclined toward the taphole, and each anode is arranged so that it can be operated independently of the others. Aluminum furnaces are built in various sizes, *e.g.*, 8 ft. long by 4 to 5 ft. wide by 2 ft. high, and generally rectangular shapes are now in use in place of the former round cells.

A set of anodes is suspended in the interior of each furnace, and these vary in size and length. Anodes are round, square, and rectangular in section, 3 to 16 in. in

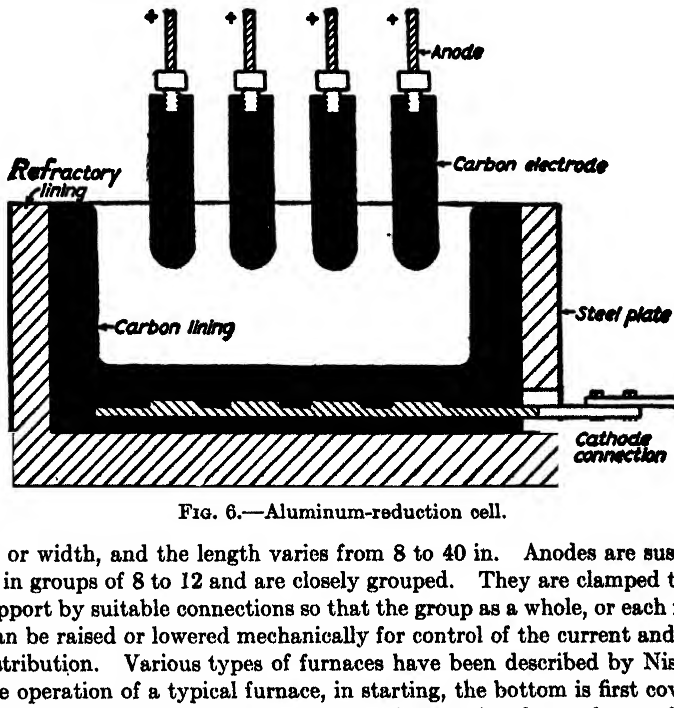

Fig. 6.—Aluminum-reduction cell.

diameter or width, and the length varies from 8 to 40 in. Anodes are suspended in the bath in groups of 8 to 12 and are closely grouped. They are clamped to a heavy frame support by suitable connections so that the group as a whole, or each individual anode, can be raised or lowered mechanically for control of the current and to ensure equal distribution. Various types of furnaces have been described by Nissen[30].

In the operation of a typical furnace, in starting, the bottom is first covered with granulated carbon shoveled in loosely, the anodes are then lowered to make contact therewith, and the current is thrown on. As the furnace heats, cryolite or a prepared bath material is added. This melts, and the anodes are raised with an increase in the bath volume, and more cryolite is added until the furnace is full. When the bath is carrying the requisite current, alumina is charged in small amounts at a time until the furnace is in full operation. Of course, other salt additions are made to the bath during the starting operation, *e.g.*, calcium fluoride and aluminum fluoride, depending upon the bath employed. Alumina is added until the bath contains 10 to 20 per cent Al_2O_3 in solution. On electrolysis, the aluminum sinks and collects on the cathode bottom, from whch it is tapped periodically, and the oxygen liberated at the anode interacts therewith. In operation, the alumina content of the bath is controlled by voltmeters and incandescent lamps connected across the terminals.

When the alumina content becomes low, the furnace voltage rises from the normal 7 volts to 15 to 20 volts. The lamps are so connected that when the bath reaches a certain resistance they light, thus giving notice to the operator.

Every two or three days, according to the capacity of the furnace, the liquid aluminum is run off through a taphole in the side. This metal is remelted in order to remove occluded bath salts and is then cast into pigs, forming the primary aluminum of commerce. First-grade aluminum contains 99 to 99.5 per cent Al (by difference). The cost of production of aluminum is now 8 to 10 cents per lb.

Manufacture of Carbon Electrodes.—Since the anodes come into direct contact with the bath, they must be as free as possible from impurities, particularly iron and silica, *i.e.*, the ash content must be extremely low, and the manufacture of anodes is an important part of modern aluminum production. Petroleum coke is the best material for anode manufacture, and in practice the coke is first crushed to small nut size and

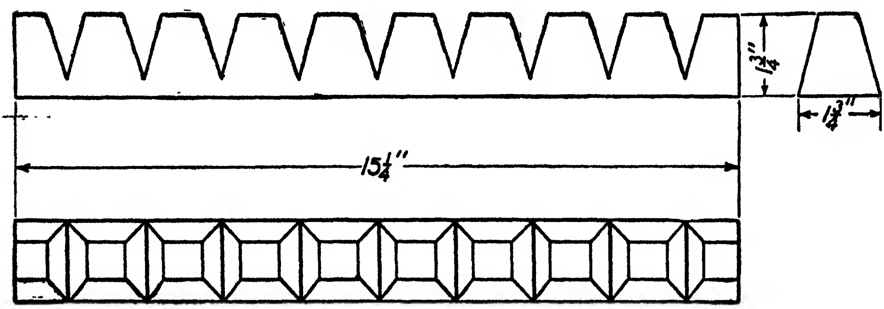

FIG. 7.—Aluminum ingot. (*British Aluminum Co., Ltd.*)

then calcined for 3 or 4 hr. at a red heat in a calcining furnace, *e.g.*, one of the Meisser type. After cooling, the calcined coke is ground, usually with waste electrodes, in a ball mill, to pass 16 to 18 mesh, of which 40 per cent passes 100 mesh. The ground coke is next mixed with a binder of pitch, or tar and oil, in steam-jacketed kneading machines, and then transferred to electrode molds or presses. The usual press is hydraulic in operation, and pressures up to 500 atm. are used.

After the electrode shapes have been formed in a press, they are air-dried and then baked in a furnace or kiln in order to remove the volatile binder. The temperature of baking is 1000 to 1400°C., depending upon the size and binder, and the heating is done slowly in order to avoid cracking. Several days are required for firing the largest sizes of electrodes. The temperature is gradually raised during the operation, and the electrodes lose about 10 per cent in weight. The furnaces are generally fired with producer gas, and the electrodes are placed in refractory saggers packed with retort-carbon powder, ground petroleum coke, or electrode scrap. Many types of furnaces are employed in baking, the common ones being the Mendheim tunnel furnace and the Meisser chamber furnace. The apparent density of petroleum-coke electrodes is 1.55 to 1.70, the real density is 1.95 to 2.05, and the ash content less than 0.3 per cent. Finished electrodes should have an electrical resistivity of about 0.0016 ohm. The production of electrodes and the apparatus used have been treated in detail by Nissen[30]. The Söderberg continuous electrode has been tried in aluminum furnaces. The Russians claim to grind a scum of carbon, alumina, and bauxite that forms in the cells with electrode material, thereby saving all of the material.

Commercial Aluminum.—The product of the reduction cell, after remelting, appears on the market as primary aluminum, and this is graded according to the amount of impurities present. The chief impurities are iron, silicon, copper, and alumina, while carbides, sulphides, sodium, nitrogen, and titanium are normally

present in very small amounts. Ordinarily, three grades of primary aluminum are marketed, *viz.:* (1) special, containing 99.5+ per cent aluminum (by difference); (2) grade No. 1 (or grade A), containing 99+ per cent aluminum; and (3) grade No. 2 (or grade B), containing 98 to 99 per cent aluminum. Primary aluminum alloys are prepared by a remelting operation in which an alloying metal is added to primary aluminum. In practice, the quality of aluminum is ordinarily based on a chemical analysis in which copper, iron, and silicon are determined, and the remainder is said to be aluminum. In 99+ per cent aluminum, the content of impurities is usually copper, trace to 0.20; iron, 0.25 to 0.60; and silicon, 0.15 to 0.40 per cent. Alumina, Al_2O_3, is a normal impurity in commercial aluminum.

Chemical Properties of Aluminum.—The chemical properties of aluminum are remarkable and of great importance. The chemical properties of the metal and its interactions with various substances have been ably discussed by Little[6] and Mellor[10] in their books, and these may be consulted for detailed information. Aluminum is very reactive chemically and under proper conditions combines readily with oxygen, the halogens, nitrogen, sulphur, and carbon; it is readily attacked by some acids, but not at all, or slightly, by others; and it is readily soluble in alkalies. The chemical properties of light aluminum alloys are, in general, similar to those of the substantially pure metal. Aluminum is a silvery-white metal with a slightly bluish tinge, and it has great coloring power, *i.e.*, it readily whitens colored metals in alloys. Aluminum forms one series of salts in which it is trivalent, and the salts are derived from the basic oxide, Al_2O_3. Aluminum salts are nonpoisonous; consequently aluminum cooking utensils are preferred to tinned steel utensils. On the basis of the ionic hypotheses, the salts of aluminum dissociate in aqueous solution, according to

$$AlX_3 \rightleftharpoons Al^{+++} + 3X^-$$

yielding the colorless cation Al^{+++}. The ionic mobility of the cation $\frac{1}{3}$ Al^{+++} is 40.4 at 18°C., according to Heyweiller. Aluminum stands high in the electromotive series. The atomic weight of aluminum is now given as 26.97 by the International Union of Pure and Applied Chemistry.

Interactions with Various Substances.—A few of the principal reactions of aluminum with various substances are indicated briefly here, and further information will be found below under Corrosion of Aluminum and Aluminum Alloys, particularly on the action of air and water. Aluminum is attacked slowly by cold acetic acid, but the rate of attack increases markedly with increasing temperature and increasing dilution of the acid. Butyric acid attacks aluminum slightly in the cold, but with boiling butyric acid the action is similar to acetic acid. Aluminum is attacked very rapidly by hydrochloric and hydrofluoric acids in all concentrations, with the evolution of hydrogen. Lactic acid has very slight effect. Cold concentrated or dilute nitric acid attacks aluminum slowly, and the metal can be employed for handling such acid. Traces of sulphuric acid in nitric acid increase the rate of attack. Oleic acid has practically no effect on aluminum. Aluminum is dissolved appreciably by hot dilute sulphuric acid, but the action of the concentrated acid is slow. Alkali hydroxides attack aluminum and its light alloys rapidly.

Aluminum interacts with carbon at high temperature to form aluminum carbide, Al_4C_3, and carbon monoxide and dioxide interact with it, forming aluminum carbide or aluminum oxide and setting free carbon. Aluminum carbide is decomposed by water, yielding aluminum hydroxide and methane. Chlorine, bromine, and iodine all attack aluminum rapidly. Nitrogen combines directly with aluminum at moderate temperature (400 to 800°C.), forming aluminum nitride, AlN. This is attacked by water, yielding aluminum hydroxide and ammonia. Aluminum reacts with ele-

mental sulphur at moderately high temperature to form the sesquisulphide, Al_2S_3; with phosphorus, to form a number of phosphides; and with arsenic, to form the compounds AlAs and Al_3As_2. Aluminum forms many chemical compounds, notably the alums, *e.g.*, $Na_2SO_4.Al_2(SO_4)_3.24H_2O$.

Oxidation of Aluminum.—The affinity of aluminum for oxygen is very great, and fine aluminum powder, or very thin foil, burns in the air, on ignition, with great violence. The thermit reduction of metallic oxides is based upon the high affinity of aluminum for oxygen. Thus, when aluminum powder is mixed with a finely divided metallic oxide and the mixture ignited, the reaction takes place with violence, yielding aluminum oxide and the metal of the metallic oxide reduced, *e.g.*,

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$$

The molecular heat of formation of Al_2O_3 is about 386,000 cal., or about 128,700 cal. per gram-atom of oxygen.

Metallic aluminum is normally covered with a thin film of aluminum oxide, and when heated in air, at temperatures up to the melting point, small particles of aluminum are gradually oxidized to aluminum oxide. Much experimental attention has been given to the oxidation of aluminum, but considerable uncertainty still exists as to the actual final end product of oxidation. Thus, several oxides, other than Al_2O_3, are mentioned in the literature. Pionchon claims that the final end product of oxidation is $Al_2O.3Al_2O_3$, indicating the existence of the suboxide Al_2O. Kohn-Abrest mentions AlO, and Al_4O_3 and Al_6O_7 have been described. All these seem unlikely. Rhodin, however, submits that substantially pure aluminum burns in air to form Al_3O_4, just as iron burns to Fe_3O_4. Aluminum quickly oxidizes if the surface is rubbed with mercury, an arborescent growth of aluminum oxide rapidly forming all over the metal. This phenomenon is known as the "activation of aluminum."

Properties of Aluminum and Aluminum Alloys.—The general physical and mechanical properties of substantially pure (commercial) aluminum have been fairly well determined, but much testing work on the properties of the light alloys is still needed. The tensile strength of aluminum is low, and the substantially pure metal finds limited and special employment for engineering construction, being valued chiefly because of its low specific gravity, great ductility, high electrical and thermal conductivity, and resistance to atmospheric corrosion. Where it is desired to take advantage of the low specific gravity of the metal, however, but where considerable strength is required, it is necessary to employ aluminum alloys.

Some excellent aluminum alloys have been developed for particular purposes, and certain of these possess tensile strength exceeding that of mild steel and the specific tenacity of alloy steels. Aluminum is malleable and ductile in the cold and can be rolled into sheet, drawn into wire, stamped and spun, and otherwise worked both hot and cold. Both the metal and its alloys are hot-short at high temperatures, and some of the alloys are cold-short.

The physical properties of aluminum and aluminum alloys are variable over a wide range depending upon the chemical composition, the physical condition, *i.e.*, whether cast or worked, and the heat-treatment. From the commercial point of view, the following properties of aluminum and aluminum alloys are of importance in particular applications: specific gravity, hardness, tensile properties at the ordinary and elevated temperatures, modulus of elasticity, compressive strength, resistance to alternating stresses and impact, thermal expansion, growth on heating, thermal conductivity, electrical conductivity; and others. To the foundryman, the following properties of aluminum alloys are of importance from the point of view of easy casting: contraction in volume and linear contraction, fluidity and viscosity, surface tension, latent heat of fusion, melting points, and some of the other properties mentioned

above. The general physical properties of aluminum have been well summarized in *Circular* 76 of the National Bureau of Standards, and valuable data are to be found in

TABLE 2.—PHYSICAL, MECHANICAL, AND OTHER PROPERTIES OF ALUMINUM[1]

Property	Units for expression	Value
Specific gravity, 20°C	Grams per cubic centimeter	2.70 ±
Specific gravity, liquid, 800°C	Grams per cubic centimeter	2.343
Solidification shrinkage	Per cent	6.6
Melting point	Degrees centigrade	658.7
Boiling point	Degrees centigrade	1800 ± 50
Thermal expansivity	Increase in length per cent of length per degree centigrade (0 to 100°C.)	0.0000239
Thermal conductivity, at 18°C	Gram-calories per cubic centimeter per 1 degree centigrade per second (c.g.s. units)	0.54
Latent heat of fusion	Gram-calories per gram	77
Latent heat of vaporization	Gram-calories per gram	2100
Specific heat	Gram-calories per degree centigrade (18 to 100°C.)	0.212
Vapor tension	At melting point in millimeters of mercury	1.0×10^{-43}
Specific electrical resistance	Microhms per cubic centimeter at 20°C.	2.82
Temperature coefficient of resistivity	Per degree centigrade (20 to 100°C.)	0.0039
Magnetic susceptibility	$H \times 10^6$, at 18°C.	+0.65
Hardness (sheet) ¼H	Brinell (10 mm., 500 kg., 30 sec.)	28
Hardness (sheet) ¼H	Scleroscope: Magnifier hammer	5–6
	Scleroscope: Universal hammer	4–5
Tensile strength (sheet) H	Pounds per square inch	13,000
Yield point (sheet) H	Pounds per square inch	8500
Elongation (sheet) H	Per cent	15
Reduction in area (sheet) ½H	Per cent	35
Modulus of elasticity	Pounds per square inch	10,000,000
Compressive strength A-132	Pounds per square inch	30,000
Linear contraction, 700 to 25°C	Per cent	1.68
Surface tension, 700°C	Dynes per centimeter	520
Heat of combustion to Al_2O_3	Calories per gram-atom of O	128,700
	Calories per gram-molecule	386,000
Heat of chlorination to $AlCl_3$	Calories per gram-molecule	180,000
Heat of sulphuration to Al_2S_3	Calories per gram-molecule	42,000
Electrolytic solution potential against calomel electrode	Volts	1.04
Atomic weight	O = 16	26.97

[1] Data collected from various sources.

the book by Girard[9]. The reports to the Alloys Research Committee of the Institution of Mechanical Engineers[18, 19, 24, 36] may be consulted for data on the physical properties of some aluminum alloys.

Table 2 gives a summary of the principal physical and mechanical properties of substantially pure aluminum; the figures may be compared with the corresponding properties for magnesium in the chapter on the Metallurgy of Magnesium and Magnesium Alloys in this work. Table 3 gives the average tensile properties of substantially pure aluminum in various forms. The tensile properties of aluminum at elevated temperatures may be determined from the formula given by the Aluminum Co. of America, *viz.*,

TABLE 3.—TENSILE PROPERTIES OF SUBSTANTIALLY PURE ALUMINUM[1]

Form	Yield point, lb. per sq. in.	Tensile strength lb. per sq. in.	Elongation on a 2-in. length, per cent	Reduction in area, per cent
Sand cast[a]	8,000– 9,000	11,000–13,000	15–25	30–40
Chill cast[a]	9,000–10,000	12,000–14,000	20–30	50–60
Sheet:				
Fully annealed	5,000– 6,000	12,000–15,000	15–30	30–40
Half hard	13,000–14,000	15,000–19,000	10–20	20–30
Hard (heavy reduction)	20,000–24,000	22,000–26,000	2–10	5–20
Bar, hard-drawn 17S-T	14,000–25,000	28,000–35,000	3–10	6–20
Wire:				
17S-T	14,000–33,000	28,000–55,000	1–10	2–20

[1] Approximate values, from various sources.

[a] But pure aluminum is rarely used for castings.

$$S_t = 14{,}107 - 32.14t$$

where t = the temperature of testing in degrees centigrade (between 50 and 400°C.), and S_t = the tensile strength in pounds per square inch at the temperature t. The solidification shrinkage of aluminum is high, 6.6 per cent.

Physical and Mechanical Properties of Aluminum Alloys.—The general physical and mechanical properties of the light aluminum alloys vary over a wide range, depending upon the composition and the condition. The extreme limits of specific gravity of the commercial alloys are about 2.4 and 3.3, and most commercial alloys have a specific gravity under 3.0. The contraction in volume of most of the alloys is high, but less than that of aluminum, and the silicon-bearing alloys have the least contraction. Experiments by the writer[60] have shown that the linear contractions of 40 alloys vary in the range 0.95 to 1.80 per cent. The melting points of the alloys range below that of aluminum down to about 575°C., the 92:8 aluminum-copper alloy melting at 636°C. While aluminum is very soft, it can be hardened greatly by alloying, and the Brinell hardness of the commercial alloys ranges from 25 to 125 (10 mm. 500 kg., 30 sec.).

The tensile strength of the light aluminum alloys varies greatly, when cast in sand, depending upon the chemical composition, and, roughly, it lies between about 14,000 and 38,000 lb. per sq. in. Chill-cast alloys are considerably superior as to strength and ductility to sand-cast ones. In castings, the strength is a function of the size of section and the pouring temperature, being less with increase of section size and increase of pouring temperature. Gillett[22] has shown that the strength of alloys poured at high temperatures may be 10 to 20 per cent less than when poured

at low temperatures. The mechanical properties of most of the light alloys are improved by either hot- or cold-working, and the best properties of one class of alloys (duralumin) are brought out only by working followed by heat-treatment and aging. Duralumin manufactures have been made with tensile strength up to 80,000 lb. per sq. in. The elongation of sand-cast aluminum alloys varies from nil to around 12 per cent. Table 3 gives the tensile and other properties for some sand-cast aluminum alloys poured at low temperature.

Few data are available as to the compressive strength of aluminum alloys, but the range is roughly 70,000 to 100,000 lb. per sq. in. At elevated temperatures, the alloys lose strength, and most are weak above 300°C. The addition of small amounts of iron, manganese, or nickel to binary aluminum-copper alloys increases their strength at high temperatures. All the aluminum alloys are exceedingly hot-short, *i.e.*, weak at temperatures immediately below the solidus. In fatigue (resistance to alternating stresses) the behavior of the alloys is variable, but the following alloys will withstand

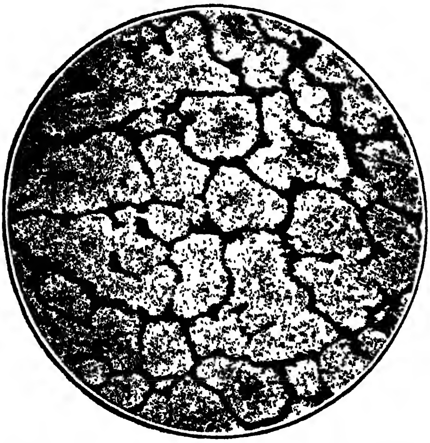

FIG. 8.—Sand-cast No. 12 alloy; etched with NaOH; × 75.

FIG. 9.—93:4:3 Al:Cu:Si alloy; × 500) (*Dix.*)

10,000,000 reversals with 7000-lb. maximum fiber stress, *viz.*, 92:8 aluminum copper; 2 to 3 per cent copper, 12 to 15 per cent zinc, and remainder aluminum; and 1.5 to 2 per cent copper, 1.5 to 2 per cent manganese, and remainder aluminum. Forged duralumin will stand 100,000,000 reversals (White-Souther) at 15,000-lb. maximum fiber stress. The Charpy impact resistance of aluminum alloys is 1 to 5 ft.-lb, notched bar, while the Izod value is 2 to 6 ft.-lb.

The coefficient of thermal expansion of the commercial light aluminum alloys varies between 22×10^{-6} and 27×10^{-6}, *e.g.*, that of the 88:12 aluminum-copper alloy is 26.4×10^{-6}, as compared with 22.31×10^{-6} for aluminum. When a light aluminum alloy is heated, it first expands, as do most metals and alloys. After reaching about 250°C., however, the increase in size becomes quite rapid and continues for some time, even though the temperature remains constant. This is called permanent growth, since on cooling down the increase in size is not lost. All the light aluminum alloys have thermal conductivity less than that of aluminum, and, generally speaking, the greater the percentage of additive elements in an aluminum alloy, the lower the thermal conductivity. Unlike cast iron, the thermal conductivity of the aluminum alloys increases with increasing temperature; that of cast iron decreases very slightly. Whereas the thermal conductivity of aluminum = 0.504, that of the

light alloys varies in the range 0.25 to 0.48, *e.g.*, the thermal conductivity of the 88:12 aluminum-copper alloy is 0.382 at 100°C. The electrical conductivity of the aluminum alloys is lower than that of aluminum, the resistivity ranging up to 5.70 microhms per centimeter cube. The electrical resistivity of duralumin is 3.35 microhms per centimeter. A most exhaustive study of the electrical properties of numerous aluminum alloys is due to Broniewski[23].

TABLE 4.—TENSILE AND OTHER PROPERTIES OF A SERIES OF SAND-CAST LIGHT ALUMINUM ALLOYS[1]

Nominal composition, elements, per cent				Elastic limit, pounds per square inch	Yield point, pounds per square inch	Tensile strength, pounds per square inch	Elongation on a 2-in. length, per cent	Reduction in area, per cent	Specific gravity	Brinell hardness[a]	Melting point, degrees centigrade	Linear contraction, inches per foot
Al	Cu	Other metals	Mg									
100	..	....	..	2,000	8,000	12,000	20	35	2.70	25	658.7	0.202
96	4	[c]	..	......	10,000	16,500	5	7	2.77	45	650	0.188
92	8	....	..	8,000	12,000	19,000	1.5	2	2.85	65	636	0.172
88	12	....	..	9,000	15,000	21,000	0.5	1	2.93	70	620	0.168
95	..	....	5	......	16,000	22,000	1.0	2	2.62	..	630	0.175
90	..	[d]	10	......	18,000	24,000	0.5	1	2.54	..	606	0.140
98	..	2 Mn	..	4,000	7,000	17,000	7	9	2.75	40	654	0.198
95	..	5 Si[e]	..	3,000	6,000	18,000	4	5	2.67	40	620	0.160
90	..	10 Si	..	5,000	10,000	20,000	2	3	2.49	50	597	0.150
87[b]	..	13 Si[f]	..	5,000	12,000	28,000	8	12	2.64	60	605	0.1[illegible]2
90	..	10 Zn	..	......	10,000	19,000	8.5	10	2.74	60	645	0.189
80	..	20 Zn	..	......	20,000	27,000	1	2	3.06	70	622	0.167
67	..	33 Zn	..	15,000	20,000	33,000	Nil	Nil	3.33		600	0.152
97	2	1 Mn	..	......	......	20,000	10	15	2.80	.	649	0.198
82	3	15 Zn	..	......	......	28,000	2	3	3.00	85	625	0.171
89.5	7.5	1.5 Fe[g] 1.5 Zn	..	......	12,000	22,000	1.5	1.5	2.85	65	635	0.168
93	4	3 Si[h]	..	......	10,000	18,000	2.6	2.5	2.80	50		
88.2	10	1.5 Fe	0.3	......	11,000	22,000	0.5	1	2.90	90	.	0.168
925.	4	1.5 Ni	2	......	12,000	25,000	2	1	2.80	70	....	0.164

[1] Data from various sources.
[a] 10-mm. ball, 500 kg., 30 sec.
[b] Modified alloy.
[c] Approximate Alcoa 195.
[d] Alcoa 220.
[e] Alcoa 43.
[f] Approximate Alcoa 47.
[g] Approximate Alcoa 112.
[h] Alcoa 108.

Many light aluminum alloys possess aging properties, *i.e.*, when freshly cast they may have their tensile properties enhanced by maturing at the ordinary temperature, and in the same way the machining properties may be improved. Thus, in foundry practice, it is usual to allow freshly cast parts of difficultly machineable alloys to age for some time at the ordinary temperature, when it will be found that they cut more satisfactorily than if machined soon after being taken out of the sand. In some alloys, the increase in tensile strength found on aging for one month after casting will be 25 to 30 per cent, but the elongation is decreased. The Brinell hardness increases on aging at the ordinary temperature. Heat-treatment enhances the strength and hardness of certain alloys most markedly. It is an accelerated aging.

Corrosion of Aluminum and Aluminum Alloys.—While it is often thought that aluminum and its light alloys are very susceptible to corrosion and that they, therefore, cannot be used for many purposes, these materials are actually more resistant to some corrosion influences, *e.g.*, ordinary atmospheric air, than are most simple

steels. The behavior of the metal and its alloys in different corroding media is, of course, very variable, and the resistance to corrosion of different alloys in the same media may be, and usually is, variable. Thus, the corrosion of aluminum or any aluminum alloy may be rapid in an acid-gas atmosphere, but slow in sea water or in ordinary atmospheric air; also, an aluminum-zinc alloy may deteriorate rapidly in sea water, while an aluminum-manganese alloy will corrode slowly.

The greater resistance of aluminum and its light alloys to ordinary corroding media, as contrasted with iron and steel, is explained by the surface coating of aluminum oxide which forms and protects against further corrosion. The corrosion of aluminum is affected by its purity, and for applications where specific resistance against corroding media is desired, the purer varieties will withstand attack better than less pure metal. Thus, the 99.9+ per cent metal made in the Hoopes cell is practically not corroded at all in dilute hydrochloric acid, while the ordinary 99+ per cent metal is rapidly attacked. Some of the light aluminum alloys, and also aluminum, when worked, are subject to corrosion cracking (season cracking)—a phenomenon familiar to brass metallurgists—*i.e.*, the materials exfoliate and crack in certain solutions, owing to internal stresses. Hard-worked aluminum corrodes more rapidly than annealed metal in general, and cast aluminum corrodes more rapidly than the hard-worked, because of minute pores in the former that give rise to local action. The corrosion of aluminum and its light alloys in various media has been described in many published papers, and only the more general aspects of the subject can be discussed here.

When aluminum and its light alloys are exposed to air, they become coated with a thin film consisting largely of aluminum oxide, Al_2O_3, or aluminum hydroxide in moist air. This film, if not broken down mechanically, serves as a protective coating, and apparently it should prevent further corrosion almost indefinitely. This film, however, may be broken readily by abrasion and other mechanical influences in service, and it is also penetrable by gases and liquids, for this reason it does not serve as an effective protection unless it is fairly thick. Aluminum is attacked slowly by fairly pure atmospheric air and more rapidly by impure air. In ordinary damp air, the oxidation may be regarded rather more as a hydration of the metal taking place simultaneously with oxidation, since in the presence of moisture, the reaction

$$Al + 3H_2O = Al(OH)_3 + 3H$$

takes place and a colloidal film of aluminum hydroxide is formed. In the presence of carbon dioxide, the oxidation of the metal takes on a pitting effect, owing to the attack of carbon dioxide on the film of aluminum oxide and aluminum hydroxide, thus revealing a fresh surface of the metal to further action.

Aluminum is not attacked by distilled water, but is attacked by tap water, impure waters, and sea water, the corrosion depending upon the constitution of the waters. Oxygen is regarded as the prime cause of corrosion of aluminum by water. It has been indicated that alkalies attack the metal and its alloys rapidly, and alkaline waters are very corrosive. Alcoholic solutions and liquors have little action, and aluminum is used in the spiritous liquor and brewing industries for containers. So-called cutting solutions and compounds used for machining aluminum and its alloys have no effect unless they contain soda ash or related sodium compounds. Ether has no corrosive action. Gasoline and oils have no action. Iron salts and compounds of iron cause a blackening of the metal. Lactic acid and milk have no action, and aluminum containers are used in dairying. Aluminum is attacked by some paints.

Protection from Corrosion.—A great deal of thought has been given to the protection of aluminum and its alloys by means of various coatings. Spar varnish was the first means used, chiefly for protecting aluminum and aluminum-alloyed parts

from sea-water corrosion on seaplanes. The "browning" process of von Grotthuss was another early method in which the aluminum part was suspended in an electrolyte consisting of a sulphur compound of molybdenum with a zinc anode and electrolyzed at 60 to 65°C. The metal was soon covered with a dark brown coating which could be rolled or bent without cracking. A process at one time popular with our Air Corps was the Z-D process of Zimmerman and Daniels[66] which consisted in treating the parts to be protected with a solution of sodium silicate followed by baking.

The chief dependence now is on anodizing, which is essentially an artificial building up of the normal aluminum oxide film to a thickness that will resist corrosion The first work on this process appears to have been done by Bengough and Stewart (British patent 223994), who made the aluminum article to be treated the anode in a chromic acid electrolyte. They also noted the ability of these oxide films to take up dyes. Certain sulphuric acid processes followed, among them being the so-called Brytal process (British patent 449162). Some further notes on anodizing will be found in the chapter on chromium.

Commercial Aluminum Alloys.—Many different alloys are now in common use. Table 5 shows a number of the standard alloys recommended by the Aluminum Co. of America, the table being based on its numbering. Because of variations produced by heat-treatment, some of the tensile strengths show a wide variation. Even the minimum values should not be used as specification limits, though ordinarily they can be depended upon. There are changes in dimensions of some aluminum alloys on aging, and most of this change can be brought about in a few hours by appropriate heat-treatment. For work requiring close tolerance, it is necessary either to allow the castings to age spontaneously or to give them a heat-treatment before machining.

It may be noted that the alloy commonly referred to as Dural is practically the Aluminum Co.'s 17S, while 24S heat-treated (24ST) is practically the European Superdural. The term "superdural" is often used to mean any low-copper heat-treatable alloy, but strictly speaking, it should refer to the alloys originally introduced by Wilm. The hardening of these alloys is due to the precipitation of a metallic compound, Mg_2Si, which occurs when the material is quenched at 480 to 500°C. and then aged. The aging may be greatly accelerated by drawing to about 100°C. The change can be delayed by keeping the material under refrigeration after quenching if subsequent forming operations are to be performed on sheets. This is now standard practice in certain plants.

Zinc duralumin is a term used to connote a class of heat-treatable alloys of the composition, for example:

	Per Cent
Copper	2.5
Magnesium	0.5
Manganese	0.5
Zinc	20.0
Aluminum (by difference)	Remainder

Zinc duralumins may be hardened by quenching followed by aging, as in simple duralumins. These alloys have been discussed by Rosenhain and his collaborators[36] The tensile properties of the alloys after working and heat-treatment are most remarkable. Rolled sheet, after quenching from 400°C. and rerolling before hardening has set in, has the following properties: yield point, 64,000 lb.; tensile strength, 75,000 lb. per sq. in.; and elongation, 10 per cent. Of special duralumins, the 92.5:4:1.5:2 aluminum-copper-magnesium-nickel alloy has been considerably exploited, and the aluminum-magnesium silicide alloy (about 1 per cent magnesium plus sufficient silicon

to form Mg_2Si) developed as the result of investigations by Hanson and Gayler has had some use. This alloy is heat-treatable and is used for sheet, bars, rods, tubing, and special shapes. It is softer and less strong than ordinary duralumin, having a strength of about 48,000 lb. per sq. in. as rolled and heat-treated as against 62,000 lb. for duralumin.

The alloy 25S is the one most commonly used for air screws, and it appears to be about the same as the German Lautal.

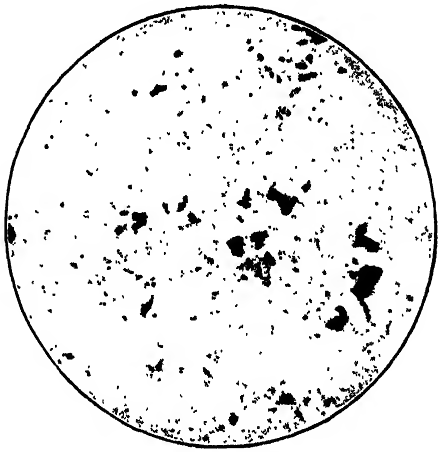

FIG. 10.—Duralumin sheet; water-quenched from 512°C. and air-aged; etched HNO_3 quench; × 200.

Casting Alloys.—Originally most aluminum castings were made in the so-called No. 12 alloy (92Al:8Cu). This alloy has been almost completely succeeded by Nos. 112 and 212 of Table 5. Number 112 is the better machining alloy, but No. 212 makes better castings. Numbers 172 and 212 are particularly recommended for thin-sectioned castings. B113 and C113 are recommended for permanent castings, as is also No. 122. This last alloy has good strength at elevated temperatures as compared with most of the aluminum alloys. Number 81 is recommended for smaller, comparatively simple die castings.

All the above are aluminum-copper alloys. The aluminum-silicon alloys are probably better casting alloys than the aluminum copper. Their fluidity and freedom from heat shortness increase to about 12 per cent of silicon, which is the Aluminum Co.'s alloy No. 13, and is apparently the aluminum silicon eutectic.

If the metal is melted under an alkaline fluoride flux, it is possible to obtain a silicon content higher than the normal eutectic composition, the castings having an extremely fine grain structure. This type of alloy is known as the "modified" alloy. The result of the treatment is largely lost on remelting.

The aluminum-silicon alloys were originally introduced by A. Pacz and are sometimes known by his name. These alloys are sometimes known in Germany as Silumin and in France as Aladar, as well as being known from their inventor as Alpax. The 12 per cent silicon alloy is reported as being used by the Germans as their chief piston alloy.

Aluminum-magnesium alloys have good mechanical properties and are particularly resistent to corrosion and tarnish. Alloys 214, B214, and 218 are recommended by the Aluminum Co. of America as considerably superior to other common sand-casting alloys of aluminum.

TABLE 5.—ALUMINUM ALLOYS IN COMMON USE
(Alloy Numbers are those of the Aluminum Co. of America. Data largely furnished by Aluminum Co. of America)

Alloy No.		Cu	Si	Mn	Mg	Zn		Fatigue limit, tons per sq. in.	Ultimate tensile strength, tons per sq. in.	Sp. gr., lb. per cu. in.
2S	W	....	....	....	....	....	....	2.5–4.3	6.5–12.0	
3S	W	....	....	1.2	....	....	....	3.5–5.0	8.0–14.5	
4S	....	....	....	....	....	....	....	3.3	9.5–12.0	0.096
11S	W[a]	5.5	....	....	....	....	Pb0.5 Bi0.5	....	6.0	
13	D	....	12.0	....	....	....	....	7.5	16.5	0.093
14S	W[b]	4.4	0.8	0.8	0.4	....	....	8.0	32.5	0.101
17S	W[b]	4.0	....	0.5	0.5	...	....	5.5–8.0	13.0–34.0	0.101
A17S	W[b]	2.5	....	....	0.3	....	....	6.75	21.5	
18S	W[b]	4.0	....	....	0.5	....	Ni2.0	7.3	27.5	0.103
24S	W[b]	4.5	....	0.6	1.5	....	....	6.0–9.0	13.0–36.0	
Alclad 24S	[b]	....	....	....	....	....	....	....	32.0–33.5	
25S	W[a]	4.5	....	0.8	....	....	....	7.5	27.5	0.101
32S	W[b]	0.9	12.5	....	1.0	....	Ni0.9	7.0	19.0	0.097
43	SC W PM D	....	5.0	....	....	....	....	3.2	9.5–12.0	0.097
45	SC	....	10.0	....	....	....	....	3.0	10.5	0.096
47	SC	....	12.5	....	....	....	....	3.0	13.0	0.096
51S	SC	....	0.9	....	0.6	....	....	....	23.5	
A51S	W	....	1.0	....	0.6	....	Cr0.25	5.3	16.0	0.097
52S	W	....	....	....	2.5	....	Cr0.25	8.5–9.5	14.5–20.5	
53S	W	....	....	0.7	1.3	....	Cr0.25	3.7–5.5	8.0–19.5	0.097
56S	W	....	....	0.1	5.2	....	Cr0.1			
61S	W	0.25	0.6	....	1.0	....	Cr0.25	4.0–6.2	9.0–22.5	
70S	W	1.0	. ..	0.7	0.4	10.0				
79	D	4.0	7.0							
81	D	7.0	3.0	....	....	....	....	8.0	16.0	0.103
82	D	14.0	5.0							
83	D	2.0	3.0	....	....	....	....	7.3	15.0	0.099
85	D	4.0	5.0	....	....	....	....	8.5	19.0	0.101
93	D	4.0	2.0	.. .	....	....	Ni 4.0	....	16.5	0.104
108	SC	4.0	3.0	....	....	....	....	4.25	10.5	0.099
A108	PM	4.5	5.5	....	....	....	....	....	14.0	
112	SC	7.0	....	....	....	1.7	Fe1.2	4.5	11.5	0.103
B113	PM	7.0	1.7	....	....	....	Fe1.2	....	14.0	
C113	PM	7.0	3.5	....	....	2.0	Fe1.2	....	15.0	
122	SC PM	10.0	....	....	0.2	....	Fe 1.2	4.7	11.5–12.5	0.103
A132	PM	0.8	12.0	....	1.0	....	Fe0.8 Ni2.5	....	18.0	0.097
138	PM	10.0	4.0	...	0.2	....	Fe1.0			
142	SC PM	4.0	....	....	1.5	....	Ni2.0	3.2–5.2	11.5–23.5	0.099
172	SC	8.0	2.5	....	....	....	....	....	11.5	0.102
195	SC	4.5	....	....	....	....	....	3.0–3.3	15.5–18.0	0.100
B195	PM	4.5	2.5	....	. ..	....	....	....	....	0.100
212	SC	8.0	1.2	....	....	....	Fe1.0	4.0	11.0	
214	SC PM	....	....	....	3.8	....	....	3.5	12.5	0.095

TABLE 5.—ALUMINUM ALLOYS IN COMMON USE.—(*Continued*)

Alloy No.		Cu	Si	Mn	Mg	Zn		Fatigue limit, tons per sq. in.	Ultimate tensile strength, tons per sq. in.	Sp. gr., lb. per cu. in.
A214	PM	....	....	..	3.8	1.8	....	....	13.5	0.096
B214	SC PM	....	1.8	....	3.8	...	....	....	10.0	
218	D	.. .	....	. .	8.0	....	.. ..	9.0	19.0	0.091
220	SC	....	.. .	..	10.0	....	....	3.5	22.5	0.092
A254	D	....		...	. .	. .	....	....	....	0.096
315	D	....	1.5	....	....	. .	....	....	....	0.097
A334	SC	3.0	4.0	....	0.3	....	....	4.3	12.5	
355	SC PM	1.3	5.0	....	0.5	....	....	4.3	12.5–21.5	0.097
A355	SC	1.4	5.0	0.8	0.5	....	Ni0.8	4.3	14.0	0.099
356	SC PM	0.2	7.0	0.1	0.3	...	Fe0.4	4.0–4.3	14.0–20.0	0.095
406	SC	....	....	2.0	....	....	....	2.8	9.5	
505	D	0.5	0.5	....	....	....	Ni4.5	....	....	0.101
645	SC	2.5	....	....	....	11.0	Fe1.2	3.8	14.5	

SC—sand casting; W—wrought; PM—permanent mold casting; D—die casting.

Ultimate tensile and fatigue limits depend on the heat-treatment and condition. The figures therefore vary widely. The upper figure is usually at maximum hardness. Permanent mold castings have higher values than sand castings.

[a] Will not age spontaneously; requires heat-treatment.

[b] Ages spontaneously. Fabricate or refrigerate immediately after quenching.

English practice has largely developed around the use of aluminum-zinc alloys, which are represented in Table 5 by alloys 112, C113, A214, and 645. There has been prejudice in the United States against the use of the zinc alloys largely because of the labor difficulties of keeping high-zinc scrap separate from zinc-free material.

The aluminum-nickel alloy (95.5 Al:4.5 Ni) is used for die castings. The 92½ Al, 4 Cu, 1½ Mg, 2 Ni is used for sand and permanent mold castings, particularly cylinder heads; it has a good strength at elevated temperatures and good bearing characteristics (alloy No. 142). This alloy is the one often referred to as the "Y" alloy of the English National Physical Laboratories.

Melting Practice.—Aluminum and aluminum alloys are melted in various types of furnaces in practice, and there is really no standardized mode. In foundry practice, light aluminum alloys have been melted in all types of furnaces that have been used for brass and bronze, and the iron-pot furnace, so widely used for melting so-called white metals, is the only one employed for aluminum alloys that is not used for brass and bronze. While a great variety of furnaces are in commercial use, as indicated, the iron-pot furnace is generally preferred for melting aluminum alloys in foundry practice and the reverberatory-type furnace for aluminum in rolling-mill practice. The theoretical and practical aspects of aluminum and aluminum-alloy melting have been discussed at length by R. J. Anderson in published papers[37, 38, 43, 50], which may be consulted for detailed information.

One of the principal difficulties in aluminum and aluminum-alloy melting is the prevention of oxidation (dross) losses, and even with the best practice there is always considerable loss. In practice, the metal and its alloys should be heated only to the required pouring temperature or a little higher, and "soaking" of melts should be

avoided. The pouring temperature for aluminum in casting rolling ingots is preferably 700 to 750°C., while in sand practice the pouring temperature may vary between 700 and 800°C., depending upon the type of casting.

Types of Furnaces and Operation.—In foundry practice, the following types of furnaces are employed in the United States: coal-, oil-, and gas-fired reverberatory furnaces; oil- and gas-fired stationary and tilting iron-pot furnaces; coal- and coke-fired stationary and tilting crucible furnaces; oil- and gas-fired open-flame tilting, rotating, and stationary furnaces; and electric furnaces of several types. In general, ordinary brass-melting furnaces of various types have simply been adapted for

TABLE 6.—TYPICAL TENSILE PROPERTIES OF WROUGHT ALUMINUM ALLOYS AT ELEVATED TEMPERATURES
(Courtesy Aluminum Co. of America)

	Temp., °F.	Strength, lb. per sq. in.		Elongation, % in 2 in.		Temp., °F.	Strength, lb. per sq. in.		Elongation, % in 2 in.
		Yield	Tensile				Yield	Tensile	
24S-T	75	45,000	68,000	22	2-0	75	5,000	13,000	45
	300	35,000	42,000	21		300	3,500	7,500	65
	400	23,000	28,000	25		400	3,000	6,000	70
	500	10,000	14,000	40		500	2,000	3,500	85
	600	6,000	7,500	65		600	1,500	2,500	90
	700	3,500	4,500	100		700	1,000	1,500	95
A51S-T	75	40,000	47,000	20	112	75	14,000	23,000	1.5
	300	15,000	19,000	28		300	24,000	25,000	1.5
	400	5,500	7,500	58		400	15,000	19,000	1.5
	500	4,500	5,500	59		500	10,000	15,000	3.5
	600	3,500	4,500	60		600	4,500	6,500	20.0
	700	3,000	3,500	65					
52S-T	75	33,000	39,000	20	122	75	30,000	36,000	1.0
	300	22,000	25,000	17	T-61	300	30,000	35,000	1.2
	400	10,000	13,000	30		400	16,000	22,000	2.0
	500	3,500	6,000	70		500	5,000	10,000	6.0
	600	2,500	5,000	75		600	4,500	8,000	14.0
	700	2,000	2,500	90					

aluminum-alloy melting, while in aluminum rolling-mill work reverberatory and open-flame barrel-shaped furnaces have been largely employed. As indicated, the iron-pot furnace is preferred for melting aluminum alloys in founding, but open-flame furnaces are being used more widely than a few years ago.

In small foundries, and in plants where only a minor part of the output is in aluminum alloys, pit or crucible furnaces are employed largely. The electric-furnace melting of aluminum and its light alloys is receiving considerable attention, and a few installations have been made. The tendency toward the employment of furnaces of large capacity, *i.e.*, reverberatory and open-flame barrel furnaces, necessarily came through the enlargement of plant capacity.

Turning to the question of oxidation losses on melting aluminum and its light alloys—when heated in air, aluminum oxidizes to aluminum oxide, Al_2O_3, and the

rate of oxidation increases rapidly with increasing temperatures. Hence, one of the cardinal rules in melting practice is that the melting temperature should be kept

TABLE 7.—COMPARATIVE MECHANICAL, ELECTRICAL, AND OTHER PROPERTIES OF ALUMINUM AND COPPER[1]

Property	Aluminum	Copper
Specific gravity	2.70 ±	8.89 ±
Melting point, degrees Centigrade	658.7	1083
Specific heat (water = 1) at 20°C., calorie	0.214	0.095
Specific thermal conductivity, calories per degree Centigrade, per square centimeter per centimeter	0.504	0.895
Approximate relative heat conductivity (silver = 100 per cent)	50	90
Coefficient of linear expansion, per degree Centigrade	0.000024	0.000017
Tensile strength, hard-drawn wire (No. 10 S.w.g.) pounds per square inch	26,000	50,000
Tensile strength, annealed wire (No. 10 S.w.g.), pounds per square inch	14,000	29,000
Modulus of elasticity, pounds per square inch	10×10^6	17.5×10^6
Specific resistance in microhms per cubic centimeter at 20°C.:		
Annealed	2.8159	1.7241
Hard-drawn	2.8735	1.7585
Specific resistance in microhms per cubic inch at 20°C.:		
Annealed	1.1086	0.6788
Hard-drawn	1.1313	0.6924
Ohms per mil-foot at 20°C.:		
Annealed	16.939	10.371
Hard-drawn	17.285	10.578
Resistance of solid conductor, 1,000 yd. long by 1 sq. in. cross-section, ohms:		
Annealed	0.0399	0.0244
Hard-drawn	0.0407	0.0249
Coefficient of increase of resistance with temperature, degree Centigrade	0.00390	0.00393
Weight per 1,000 yd. by 1-sq. in. cross-section, pounds	3,510	11,520
For hard-drawn conductors of equal resistance:		
Ratio of diameters	1.28	1.0
Ratio of sectional areas	1.64	1.0
Ratio of weight	0.5	1.0
For hard-drawn conductors of equal temperature rise:		
Ratio of diameters	1.18	1.0
Ratio of sectional areas	1.39	1.0
Ratio of weight	0.424	1.0

[1] According to the British Aluminium Co., Ltd.

low, and, moreover, heats should not be allowed to soak in the furnace. The oxidation product resulting on melting is known as "dross," and this ordinarily contains some

mechanically entangled metal, the percentage depending upon the care used in skimming the melts. In addition to the temperature, the constitution of the furnace atmosphere in which the metal is melted is of great importance, because of interactions that take place. Thus, in addition to reacting with oxygen, aluminum reacts with nitrogen at normal melting temperature, forming aluminum nitride, and this appears in the dross. Hence, when a furnace is operated with a great excess air supply, the dross loss is necessarily high.

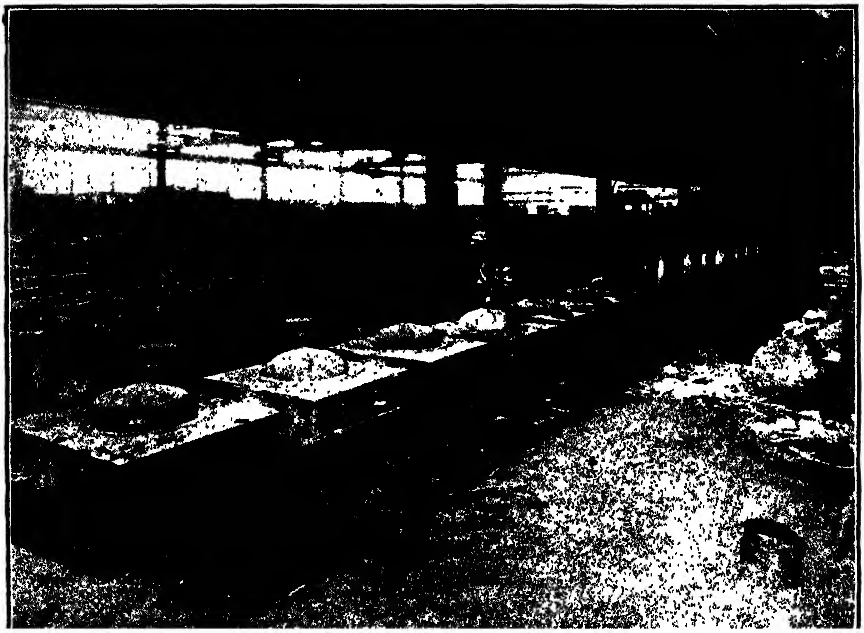

FIG. 11.—Stationary iron-pot furnaces in a foundry.

Alloying Practice.—Prior to the production of any kind of aluminum-alloy manufactures, it is first necessary to prepare the required alloys, and, in practice, the alloys may be prepared and used immediately or they may be prepared and cast into pig form for subsequent remelting. As a rule, founders prefer to make up the alloys as required rather than to purchase prepared alloys. Primary aluminum alloys of definite compositions are sold in ingot form for casting purposes, and a tremendous tonnage of secondary aluminum-alloy pig is made and sold. Primary aluminum alloys, whether pigged or used directly for casting, are made up by adding the alloying metal or metals to aluminum in a melting operation, while secondary aluminum alloys are made by running down scrap aluminum and aluminum alloys.

Foundry practice in making up alloys for casting varies considerably, and melting charges may consist of the following: (1) all-primary aluminum pig plus the necessary alloying metal, or intermediate alloy required for introducing the additive metal, plus foundry scrap or not; (2) primary aluminum-alloy pig plus foundry scrap; (3) primary aluminum, intermediate aluminum alloy, foundry scrap, and secondary metal; (4) all secondary metal plus foundry scrap. Other combinations have been employed, and these will readily suggest themselves. In making aluminum-copper alloys, it is usual to make a fixed addition of copper to the aluminum by the use of the intermediate copper-aluminum alloy of nominal composition 50:50 copper-aluminum, known in

foundry practice as "hardener." Pure copper and 33:67 and 60:40 copper-aluminum alloys are also employed. The preferred order of adding alloying elements to aluminum is copper, silicon, iron, amnganese, and magnesium.

Iron may be introduced into aluminum alloys by the use of light scrap tin plate or ferroaluminum, although the avoidance of iron is usually a more important problem than its addition, while magnesium is best added in small pieces as pure magnesium, using a perforated crucible or "phosphorizer" for containing the metal. Manganese additions are usually made with 25:75 manganese-aluminum alloy, and nickel as light sheet nickel or 20:80 nickel-aluminum alloy. Silicon is added preferably by using the 50:50 silicon-aluminum alloy. Zinc, tin, and other low-melting-point metals are added as such. An intermediate alloy is essential when high-melting-point metals are to be alloyed, and the employment of these intermediate alloys is a great convenience. Most of them are brittle and can be weighed with accuracy, and their melting points are low, so that the additive metal can be introduced readily without long or high heating. Manganese may also be introduced by the use of manganese chloride in the flux. Zinc chloride in small amount is used extensively in melting and alloying practice for aluminum and its light alloys, with the object of cleaning and fluxing the melts. It is efficacious for the purpose.[59].

Secondary Aluminum and Aluminum Alloys.—Secondary aluminum is produced by remelting aluminum scraps and is used largely for remelting in foundry practice for making alloys, although some secondary metal is employed for the production of aluminum rolling ingots. Secondary aluminum alloys are made by remelting aluminum and aluminum-alloy scraps, and such alloys are used largely in foundry practice. In the remelting of aluminum-bearing scraps no refining can be done, as in the case of copper, and, consequently, secondary aluminum and aluminum alloys are normally less pure than the corresponding primary materials. The usual impurities found in secondary aluminum include copper, iron, silicon, manganese, and zinc, while secondary aluminum-alloy pig, say No. 12 alloy, may contain iron, silicon, manganese, magnesium, tin, and zinc, in addition to copper.

While all sorts of aluminum scraps are utilized in making the secondary metals and alloys—including aluminum dross and skimmings, aluminum rolling-mill scrap, aluminum fabricating scrap, particularly from utensil plants, and the corresponding aluminum-alloy scraps—the bulk of the secondary aluminum-alloy pig is produced by smelting aluminum-alloy machinings from aircraft and ordnance plants. Considerable heavy aluminum-alloy scrap results from the junking of old motor cars, and this makes good material for remelting. In machining castings, about 25 per cent of the weight is removed. In cutting and working sheet aluminum, about 20 per cent ordinarily goes into scrap. Considerable amounts of aluminum dross and aluminum-alloy dross are smelted in secondary practice. In drosses, the content of metallics may run 5 to 60 per cent, depending upon conditions, and the recovery on smelting varies from 40 to 75 per cent. The recovery on smelting borings may be 40 to 90 per cent of the metal charged, and 80 per cent is good recovery on dirty borings. Recovery naturally depends upon the quality and size of borings, *i.e.*, as to whether the chips are oily, dirty, or clean, and whether large or small[67].

A recent proposal for scrap treatment has been put out by the Aluminum Co. of America. Aluminum aircraft scrap is to be introduced in a bath of sodium hydroxide which will dissolve the aluminum, and the solution is to be treated by the Bayer process, leaving everything else behind. G. C. Riddell has put forth the objection that zinc would also dissolve, thus contaminating the solution. The proposal was to treat it as an ordinary Bayer-process liquer.

The question of fluxes to be used in secondary aluminum work is of great importance, and a great number have been suggested, although only a few have been

extensively employed in practice. The object in using a flux is to reduce oxidation loss on melting and to cause coalescence of the metal, particularly when melting fine scraps, like borings, and drosses. In practice, the 85:15 sodium chloride-calcium fluoride flux is used most generally, but zinc chloride, several special mixtures of alkali fluorides, and cryolite are also employed. As indicated, the methods of smelting are varied, and all sorts of methods have been suggested. Heavy scrap can be readily melted with little loss, but special methods are necessary in smelting drosses, borings, and fine scraps. In running borings and drosses, the materials are often charged to a liquid heel in a crucible furnace with a flux, and the mass puddled to ensure coalescence of the melted globules, while recently the practice of puddling and working such materials in large reverberatory-type furnaces has gained ground. Drosses are normally crushed and screened to remove aluminum oxide before smelting, while borings should be run over a magnetic separator to remove included iron chips. Light scrap, like that from utensil fabrication, may be economically baled before smelting.

Aluminum Foundry Practice.—Cast-iron crucibles are very largely used in aluminum foundries. The crucible should be completely emptied each day (and sometimes oftener) and a wash given with a suspension of 7 lb. of whiting per gallon of water. Superior adhesion of the whiting to the metal can be obtained by adding 4 or 5 oz. of sodium silicate to each gallon of the mixture.

Graphite and clay crucibles are sometimes used, particularly if aluminum-silicon or aluminum-magnesium alloys are to be made, as their use minimizes any iron pickup. On the other hand, the molten metal has a tendency to pick up silicon if there is any in the crucible. Covers should be used on all crucibles in order to minimize the absorption of gas from the products of combustion.

It is impossible to judge the temperature of molten aluminum by its color as can be done with some other metals, so that some form of pyrometric control must be used.

Some good advice was contained in a paper on recommended practice for casting sponsored by the Aluminum and Magnesium Committee on Sand Castings of the American Foundrymen's Association, read at the annual meeting in St. Louis in 1944. Aluminum should be poured at the lowest temperature at which the casting will run and allow air bubbles and dross to escape from the metal. Melting temperature should also be kept low to prevent the formation of oxide and the absorption of furnace gases. Agitation of the molten metal either in the furnace or while being taken to the mold increases oxide formation and gas absorption. Continual skimming of the ladle increases the loss as oxide, since each time the protective coating is removed a new one forms. If the metal must be stirred, it should be done from the bottom upward, disturbing the surface as little as possible. Pouring time should be kept as short and with as few breaks as possible. The ladle should be kept as close to the sprue as possible, as too great a pouring height results in dross and trapped air in the final casting.

In general, temperatures in excess of 1300°F. for metal melted in direct-flame furnaces and 1500°F. for metal melted in indirect-flame furnaces are to be avoided. Metal that has been heated at too high a temperature and that has as a result absorbed too much gas does not give this out again even on prolonged standing, and metal that has become thoroughly gassed should be poured into ingots and remelted.

Molding Sand and Core Sands.—For green sand work a clay-bonded sand free from organic matter and falling within the A.F.A. classification 1G to 2G should be used. The finer sand is best for small benchwork and the coarser sand for floor work. A typical Albany sand has the following analysis: loss on ignition, 1.95; SiO_2, 80.52; Fe_2O_3, 4.83; Al_2O_3, 8.39; CaO, 0.67, MgO, 0.64; alkalis, 2.7. Sand of the above type mixed with 6 to 8 per cent water and lightly rammed gives a good surface to the castings and is open enough to permit the escape of the mold gases. Cores are made

of silica sand and sometimes molding sand held together with linseed or tung oil, while resin, dextrin, flour, or combinations of these materials are used. A table furnished by the Aluminum Co. of America gives some typical mixes. An interesting basis for the classification of foundry sands will be found in a footnote on pages 62 to 63. In general, aluminum foundry sand should fall in the classification 1G to 2G.

A notable grain refinement can be produced in aluminum by the use of small quantities of columbium and titanium. In the case of columbium $\frac{2}{100}$ to $\frac{10}{100}$ per cent produces good results. With titanium up to $\frac{15}{100}$ per cent can be profitably used. Too much must not be used, for if $\frac{3}{10}$ per cent of either of these elements is used the results become distinctly detrimental[75].

Apart from the solid fluxes such as the chlorides and fluorides, nitrogen gas and chlorine gas are also used in aluminum foundry practice. They are usually piped to

TABLE 8.—TYPICAL CORE SAND MIXES FOR ALUMINUM-ALLOY CASTINGS

Sands, parts by volume	Binders, parts by volume	Physical properties		General use
		Approx. A.F.A. permeability	Approx. A.F.A. compressive strength, lb. per sq. in.	
50 Bank sand 50 Washed silica sand[a]	1 Oil base 1 Dextrin base (dry bond)	50	200	Small to medium castings requiring very smooth surfaces
100 Washed silica sand[b]	1 Oil base 1½ Dextrin base (green bond)	150	550	Jacket cores and cores with thin sections
66 sharp sand 34 Bank sand	1½ Oil base	85	350	General runs of small cores
37 Bank sand 63 Burned core sand	2 Pitch base	40	100	Large body and housing cores
25 Bank sand 63 Burned core sand 12 Molding sand	3 Dextrin base (dry bond)	25	325	Side cores in contact with metal on one side only

SAND CHARACTERISTICS

Sand	Grain shape	Grain fineness
Bank sand........	Subangular	90
Washed silica sand	Rounded	85
Washed silica sand	Rounded	65
Sharp sand.......	Angular	55
Molding sand.....	Subangular	270

[a] Grain fineness, 85.
[b] Grain fineness, 65.

the bottom of the melting pot and allowed to bubble gently up through the metal. These gases must be free from water vapor, hydrogen, or oxygen.

If solid fluxes are used, the required amount can be determined by sprinkling a small quantity of the flux on the molten metal, stirring it into the dross, and continuing to stir in small amounts until the dross becomes powdery and granular, in which state it can be readily removed with a perforated skimmer.

Gates and Risers.—The gates and risers used in aluminum castings are much larger than those used in other nonferrous work. As laid down by the Aluminum Co. of America, castings should be gated and fed in such a way as to provide a sequence of solidification that ensures an adequate supply of molten metal to feed each section as it solidifies. The solidification should start at points furthest removed from the gating area and proceed progressively to the risers which provide liquid metal to take care of the shrinkage.

Casting Defects.—Of the various defects that may occur in sand castings of aluminum alloys, the three most frequent and important are: (1) blowholes, porosity, and general unsoundness; (2) hard inclusions; and (3) cracks. Blowholes are caused primarily by too high melting and pouring temperatures, and can be largely prevented, but general unsoundness is more difficult to overcome. As a rule, aluminum-alloy sand castings tend to be unsound, and in practice it is necessary to make tests on inspection, in certain types of castings, for porosity and related defects.

The usual method employed for detecting general or local porosity in such castings as crankcases, oil pans, manifolds, etc., is the open test with a solution of methylene blue in gasoline. In the test, this liquid is painted or smeared on the casting, and if the part is porous, the solution will seep through and show on the other side. Air-pressure, water-pressure, and steam-pressure tests are also applied, particularly to hollow castings, for detecting porosity and leaks. Porous castings may be treated, *i.e.*, the porosity closed, by several methods, of which the sodium silicate method is the one most commonly employed. In this, the castings are first soaked in concentrated (40°Bé., 1.38 sp. gr.) sodium silicate solution for an hour, then immersed for 1 to 2 min. in dilute sulphuric acid (25 per cent), and then washed in water. The casting is then dried at about 100°C. for at least 1 hr. Impregnation with tung oil is also practiced. Porous castings may also be treated with bakelite[32].

The occurrence of hard inclusions, *i.e.*, the so-called "hard spots" of foundry parlance, in aluminum-alloy castings is of interest and importance to founders and users of parts. In some cases, the percentage of machine-shop returns, owing to rejections because of hard inclusions, may be high and be the cause of considerable loss. Hard inclusions differ so widely in character that the term "hard spots" is only roughly descriptive, but hard spots are ordinarily defined as any kind of metallic or nonmetallic inclusions that cause difficulty on machining or polishing. When a machine tool strikes a hard inclusion, its edges are quickly dulled and rendered unfit for cutting. All hard inclusions may be divided into two classes, *viz.*, (1) nonmetallic inclusions and (2) metallic inclusions. Under the former are included all hard, foreign, nonmetallic particles, such as pieces of brick or cement, chunks of crucibles, core sand and molding sand, and hard clay, that may be charged with the melting stock. Metallic hard inclusions are generally traceable to iron and are due to actual iron or steel, such as nails, core wire, chaplets, or chills, charged into the furnace, or to the hard intermetallic compound $FeAl_3$ caused by the dissolution of iron or high iron in the melt. The subject of hard inclusions in aluminum-alloy castings has been discussed at length by the writer[45]. They can be practically entirely prevented by clean melting practice.

Cracks in aluminum-alloy castings constitute the most serious defect encountered in founding, and if the average casting loss is taken as 10 per cent, the wasters because

of cracks amount to 2 per cent of the castings poured, or 20 per cent of the total defectives. The usual commercial aluminum alloys are subject to cracking when poured into molds, owing to their large contraction in volume on freezing and their hot-shortness, and, so long as complicated castings are made, cracks must be expected in production. Some of the principal factors affecting the occurrence of cracks are the composition of the alloy; the method of molding; and the design of the castings, particularly as to thick and thin sections in contiguity. In general, the less the contraction in volume of the alloys, the less the cracking. The silicon-bearing aluminum alloys are particularly good for casting, since they have little tendency to crack—their contraction in volume is relatively low as compared with the other alloys. The causes of, and methods for the prevention of, cracks have been discussed by the writer in another place[53], where detailed information will be found.

Die Casting and Permanent-mold Casting.—Aluminum-alloy castings are made in large quantity by two other processes than sand casting, *viz.*, by die casting and permanent-mold casting, but this subject does not appear to fall within the scope of this book.

Forging.—Aluminum and its alloys crack and blister when forged at too high a temperature. The maximum temperatures at which forging should be carried on are as follows: 14S, 17S, 70S, 840°F.; 18S, 73S, 820°F.; A51S, 53S, 880°F.; 25S, 860°F.; 32S, 800°F. The upsetter heat for 14S is 800 to 900°F. The upsetter heat for 32S is 880 to 900°F.

Heat-treatment.—Both wrought and cast aluminum alloys are heat-treated commercially, and a wide field has thus been opened. Worked aluminum is annealed, as are the alloys, for the purpose of softening, and some cast alloys are annealed to release casting strains. Aluminum-alloy pistons are annealed to overcome growth and distortion. That alloys of the duralumin type are heat-treatable has been known since the investigations of Wilm in 1903, and the phenomena involved are common to many alloys. In a general way, the heat-treatability of aluminum alloys is due to the varying solubility of metallographic constituents with temperature, *e.g.*, $CuAl_2$ in aluminum-copper alloys and duralumin and Mg_2Si in duralumin. When such alloys are heated to moderately high temperature, *e.g.*, 500°C., more of the constituents go into solution, and, when quenched, these constituents at first remain in solution but on standing precipitate out in particles of very high dispersion. Consequently, hardening and strengthening ensue.

Worked aluminum and aluminum alloys are softened by simple anneal at 350 to 500°C., depending upon the amount of reduction and the time period of anneal. Certain cast aluminum alloys, *e.g.*, 95:5 aluminum-copper alloy, are suitable for quenching heat-treatment, and this is now being employed somewhat in practice for enhancing the properties of sand castings. The strength of the rolled and annealed 95:5 aluminum-copper alloy is increased from about 27,000 to 52,000 lb. per sq. in. by quenching and aging. When duralumin is quenched from about 500°C., it is soft and ductile, but on aging at the ordinary temperature for a few days the hardness and strength increase markedly while the elongation falls off. The aging may be accelerated by heating at 100 to 200°C. for 1 to 5 hr. The heat-treatment of duralumin has been discussed by a number of workers, including Merica and his collaborators[33*a*], Hanson[35], Rosenhain[56] *et al.*, Konno[42], Knerr[48], and many others. The hardening and strengthening on heat-treatment are due to the precipitation of $CuAl_2$ and Mg_2Si. In practice, heat-treatment is applied principally to worked duralumin, and the heating is carried out under careful pyrometric control in any suitable furnace. The quenching medium may be cold water, boiling water, or oil. Parts may be heated for quenching in a salt bath, *i.e.*, a mixture of potassium and sodium nitrates. Since quenched duralumin is soft, the material may be quenched

in water, then immediately worked to the required shape, and then allowed to age. Zinc duralumin is heat-treatable, as is the 92.5:4:1.5:2 aluminum-copper-magnesium-nickel alloy. Heat-treated duralumins have been used very largely in aircraft construction, though more abroad than in the United States.

Soldering and Welding.—The soldering of aluminum and aluminum alloys has attracted a great deal of interest on the part of laymen, and many patents have been taken out for solders and soldering fluxes purported to be suitable for joining aluminum and aluminum-alloy parts. Most of these are entirely useless. Aluminum parts can be soldered together fairly easily, provided the proper precautions are taken, but in all cases, irrespective of the solder employed, the joint is not permanent and fails after a short time on exposure to moisture or humid atmospheres. Joints fail because all the metals used in solders are electronegative to aluminum, and in the presence of water galvanic couples are formed, so that disintegration takes place by electrolytic corrosion. Soldering should never be done if the joint is to be exposed to moisture or if it must withstand stresses. Soldering may be regarded as satisfactory if it is desired simply "to stick parts together" and no permanence is required. While welding is the only method to be recommended for joining aluminum and aluminum-alloy parts where the joint is exposed to the weather or must be strong, still in practice it is often desired to solder, *e.g.*, in repairing slight defects in castings or in making small repairs on aluminum parts. The essential features of soldering and welding are discussed briefly below.

The limitations of soldering aluminum and its alloys have been thoroughly discussed[63], and soldering should certainly have very limited application in aluminum work, and it never should be used for the assembly of structures. Aluminum solders usually consist of low-melting-point alloys of zinc, tin, and aluminum, although many complex alloys have been suggested, containing copper, lead, iron, bismuth, antimony, and other metals in addition. The function of metals other than zinc, tin, and aluminum in a solder is not clear, and practically any other added metal is of no use, if not harmful. Most commercial aluminum solders that are useful contain 40 to 80 per cent tin, 10 to 50 per cent zinc, and 0 to 10 per cent aluminum, and the melting range is about 200 to 500°C. Their strength is 6,000 to 14,000 lb. per sq. in. and elongation 2 to 20 per cent. A ductile solder is desirable, and the presence of copper or antimony, or excess of aluminum, which causes brittleness, is to be avoided. Normally, the strength of soldered joints is not equal to the strength of the solder, and failure may occur through the solder and at the joint on breaking.

While various fluxes are recommended for soldering, these are unnecessary, and soldering may be conveniently carried out as follows: The surfaces to be soldered are carefully cleaned with a file or emery paper, and are then "tinned" or coated with a layer of the solder by heating the surface and rubbing the solder into it. The joint between the "tinned" surfaces is then made in the ordinary way with a soldering iron and the solder. In giving the preliminary coat of "tin" to the surface, the solder may be rubbed in thoroughly with a wire scratch brush. Soldering may also be carried out by first electroplating the surfaces, and the joint depends upon the firmness with which the electrodeposited metal adheres to the aluminum. Copper plating is sometimes used. Where soldering is done directly without electroplating, the effectiveness of the joint depends upon the adhesion between the aluminum and the initial layer of solder.

As indicated, the applications of soldering to aluminum and its alloys are limited Soldering should never be used for structural assembly, but it is useful for making. repairs on defective castings in the foundry[63], *e.g.*, in filling up small holes, blows, draws, etc. It shoud not be applied in building up large bosses or lugs, but is not dangerous for patching small defects that mar the appearance of an otherwise good

casting. The best solders are tin-zinc and tin-zinc-aluminum alloys; in the former, the composition is 15 to 50 per cent zinc and the remainder tin, and in the latter the composition is 5 to 12 per cent aluminum, 8 to 15 per cent zinc, and the remainder tin.

Autogenous welding by an oxygas method is employed extensively in the aluminum industry for making joints of substantially pure aluminum and aluminum alloys, for the assembly of structures, and for making repairs and salvaging castings. Aluminum sheet is welded in building up tanks and vessels for the chemical industry, and when sheets are joined, butt welding by the oxyacetylene or other oxygas process is suitable except in very light gage sheet where the edges are lap- or flange-welded. The oxygas process of welding the light aluminum alloys causes actual alloying of the parts to be joined and the welding material, and a fairly solid alloy can be obtained at the juncture if proper precautions are observed. In the assembly of structures, a number of methods, such as riveting, folding, sewing, doweling, and the like, have been replaced by welding. Autogenous welding consists in heating the two parts to be joined and then running liquid metal in at the juncture. In welding aluminum, it is useful to use an aluminum wire as the welding material, while for the light alloys a stick or rod of the same composition as the alloys is employed. In welding, the principal difficulty encountered is the removal of the aluminum oxide from the surfaces to be joined and in practice this is accomplished by chemical (fluxes) or mechanical (puddling) means. Electric-resistance and electric-arc welding are used for aluminum and its alloys in addition to the oxygas process. Particularly has aircraft work made use of spot welding, but this is a subject for a book in itself.

Many salts and mixtures of salts have been suggested for welding fluxes, but a flux that will dissolve aluminum oxide is required. The most suitable fluxes are mixtures of alkali fluorides and chlorides as patented by Schoop[76]. A good flux for welding consists of 0.124 lb. potassium carbonate, 0.33 lb. lithium fluoride, 2.53 lb. sodium chloride, and 3.0 lb. potassium chloride. While fluxes are generally used in welding aluminum, they are not favored in American practice for repairing castings, and in such work the aluminum oxide film is broken down mechanically by a puddling rod. Oxyhydrogen and oxyacetylene welding are done on both aluminum and its alloys, and the former is probably preferable. In welding aluminum sheet, *e.g.*, building tanks, butt welding is suitable and a feeder of aluminum wire is used. The surfaces to be joined are heated, and the wire covered with flux is melted in the torch and run into place, being puddled down and smoothed off. Welding thin stock requires considerable skill.

The repair of aluminum-alloy castings is usually done by oxyacetylene welding, using no flux, with a welding stick of the same composition as the castings. For small welds, the casting should be preheated with the torch over a considerable area in the vicinity of the spot to be welded, but for large welds and even small welds on complicated castings it is best to heat the entire casting to 300 to 450°C. in a preheater. The stock in the vicinity of the place to be welded is melted down with the torch, and the hole so made is filled with liquid alloy from the welding rod, also melted by the torch. The metal is then puddled and poked with an iron rod until a pool is formed which ensures thorough alloying with the body of the casting. The operation should be conducted rapidly, and excess alloy is scraped off while still pasty. Large castings should be cooled slowly in the furnace or in hot ashes after welding to avoid cracking. Heat-treated duralumin parts are welded in aircraft assemblies, and such welds should be heat-treated.

Several extensive bibliographies on aluminum and aluminum alloys have been published, and following are a few selected references to some of the more important publications on the subject. These will serve as a guide to the literature.

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CHAPTER II

MAGNESIUM AND BERYLLIUM

By Donald M. Liddell[1]

Introduction.—Magnesium is the lightest metal of the alkali-earth division of the second group and the lightest metal employed for engineering purposes of construction. Its specific gravity is 1.74. Magnesium was little used in the United States prior to 1914, and its large-scale production began in 1915 when German imports were shut off. Its development during the present war has been one of the outstanding metallurgical developments of the period. It is probable its use was about sixty times as great in 1943 as it was in 1938, say 390,000,000 lb. as compared with 6,000,000.

Historical Survey.—In 1808, Davy first made magnesium by the reduction of magnesium oxide with potassium vapor and also by the electrolysis of anhydrous magnesium chloride, but the metal obtained was very impure. In 1830, Bussy made magnesium by reduction of anhydrous magnesium chloride with potassium, and in 1852 Bunsen prepared it by electrolysis of the anhydrous chloride in a porcelain crucible, using a carbon anode and cathode. In 1856, Matthiessen produced the metal by electrolysis of a liquid (fused) mixture of magnesium chloride and potassium chloride (4:3) plus a little ammonium chloride. The first industrial production was undertaken in France by Deville and Caron in 1863. Their process entailed reduction of a mixture of anhydrous magnesium chloride and calcium fluoride by metallic sodium, using closed iron crucibles as the containing vessels. Deville showed also at this time that magnesium could be distilled in an atmosphere of hydrogen, and he prepared very pure metal by this process.

Later, Sonstadt introduced improvements in the Deville-Caron process, whereby the metal was made by reduction of a mixture of magnesium chloride and sodium chloride with sodium in iron retorts, followed by distillation of the resulting impure metal. In 1885, von Püttner produced magnesium by a process closely resembling zinc retorting. In the process, a magnesium mineral (*e.g.*, magnesite) is first converted to the oxide, and this is reduced by carbon in heated retorts, the reduced magnesium distilling and being condensed. A number of patents were taken out after 1880 for processes specifying electrolysis of magnesium salts, both aqueous and fused, and for the reduction of magnesium compounds to metal by carbon, aluminum, etc., but these cannot be considered here. In the ordinary electrolytic process, which was developed in Germany and which supplanted Sonstadt's method, an anhydrous fused electrolyte having the composition $MgCl_2.KCl.NaCl$ (or other mixture of the three chlorides) is electrolyzed in iron cells using carbon anodes, the iron of the cells forming the cathode. In this process, the magnesium is dissociated by the current, floats on top of the bath, and is ladled off. This was the principal process employed in Germany prior to the war, and the same process or a modification thereof is still employed by several producers. The first production in the United States was apparently by a company that existed in Boston from 1865–1892 and which used the Sonstadt method, but it was a small production chiefly for flashlight purposes. The first production on

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a large scale in the United States was probably by Cunniff Bros. (the Rumford Metal Co.), at Rumford Falls, Me., in 1914–1915, using electrolysis of the fused chloride.

In the interval between the First and Second World Wars a process was developed for the electrolysis of magnesium oxide dissolved in a fluoride bath (strictly analogous to the Hall-Héroult process for the production of aluminum), and this period also was marked by the rise of processes depending on the reduction of magnesium oxide by carbon, by carbides, silicides, and aluminum; these new processes will be described in some detail further on.

Magnesium Sources, Ores and Minerals.—The ores, or raw materials, for the production of magnesium are extremely widely distributed, and magnesium is the fifth most abundant metal in the earth, following silicon, aluminum, iron, and calcium in the order named. Magnesium constitutes 2.24 per cent of the earth's crust (Clarke). Unlike aluminum-mineral deposits, which are found only fairly frequently in suitable composition and tonnage for the production of aluminum by electrolytic processes, magnesium deposits, notably magnesite and dolomite, occur in large amounts, widely distributed, and of suitable quality for magnesium production. Magnesium salts, notably the chloride, double chlorides, and sulphate, are found in salt beds and are constituents of saline springs, salt lakes, and the ocean.

Magnesium is never found native. Table 1 shows the chief sources of magnesium.

TABLE 1.—MAGNESIUM CONTENT OF VARIOUS SOURCES OF THE METAL

Mineral	Composition	Approximate per cent magnesium
Dolomite........	$MgCO_3.CaCO_3$	13
Serpentine.......	$3Mg.2SiO_4.2H_2O$	25
Olivine..........	$(Mg, Fe)_2SiO_4$	28
Magnesite.......	$MgCO_3$	28
Brucite.........	$Mg(OH)_2$	41
Hydromagnesite.	$3MgCO_3.Mg(OH)_2.3H_2O$	26
Kieserite........	$MgSO_4.H_2O$	14
Kainite.........	$MgSO_4.KCl.3H_2O$	9
Carnallite.......	$MgCl_2.KCl.6H_2O$	8.7
Langbeinite.....	$2MgSO_4.K_2SO_4$	11
Spinel...........	$MgAl_2O_4$	17
Talc............	$H_2Mg_3Si_4O_{12}$	20.7–26.9
Serpentine.....	$H_4Mg_3Si_2O_9$	26
Sea water.......		.13
Brines..........		Variable

In igneous rocks, magnesium is represented by amphiboles, micas, pyroxenes, and olivine. Talc, chlorite, and serpentine are common magnesium silicates, and dolomite is frequently found in enormous mountain masses. Magnesite is mined in Australia, Austria, Hungary, Czechoslovakia, British India, Canada, Greece, Italy, Spain, South Africa, and in the Pacific coast states of California and Washington. Dolomite is mined in California, Colorado, Illinois, Ohio, Pennsylvania, and West Virginia, and various foreign countries. The sulphate ($MgSO_4.7H_2O$) is one of the principal saline constituents of many springs. There is a peculiar deposit of pure magnesium sulphate at Basque, B. C., and this salt is obtained commercially from a dry-lake deposit near Oroville, Wash., and from the bitterns of certain California salt works. Massive magnesium fluoride is mined in Italy.

In oceanic salts, magnesium chloride makes up about 11 per cent of the total salt content, and oceanic water contains about one-eighth per cent magnesium, so that at 100 per cent recovery, it would require about 200,000 gal. of sea water to produce 1 ton of metallic magnesium. Magnesium-bearing bitterns are found at San Mateo, Calif.; Syracuse, N. Y.; Pomeroy, Ohio; Hartford, W. Va.; in the Saginaw Valley of Michigan, notably at Midland; in Colombia; in Germany; and elsewhere. The magnesium content of some inland salt lakes is high, notably Great Salt Lake, Utah, which contains 0.56 per cent magnesium. Houghton Lake, at Dana, Saskatchewan, is underlain by a 1 ft. thick layer of salts, chiefly magnesium sulphate and sodium sulphate. The principal and most famous salt-bed deposits containing magnesium minerals are the great Stassfurt salt beds in Germany (Magdeburg-Halberstadt region). The principal magnesium-bearing minerals of these beds are carnallite, $MgCl_2.KCl.6H_2O$, bischofite, $MgCl_2.6H_2O$, and tachydrite, $2MgCl_2.CaCl_2.12H_2O$. Magnesium-bearing salt beds also occur in Spain, Alsace, and the United States.

While minerals and ores of magnesium are abundant, in practice raw materials for production of the metal are obtained from only a few sources. These are anhydrous sodium-magnesium chloride, left after extraction of salt and bromine from brines at Midland and Ludington, Mich.; carnallite from Stassfurt; magnesite (notably from California); and magnesium carbonate, precipitated from dolomite, and some experimental production from olivine. Magnesium is made from magnesium oxide obtained from sea water in the United States, Great Britain, Italy, and Japan. Magnesium chloride is a by-product of the preparation of potassium salts in Germany and in New Mexico and can be made very cheaply. The magnesium content of magnesite as mined averages 25 per cent and that of carnallite 8 per cent.

Production of Magnesium.—Many processes for the production of magnesium have been patented, suggested, or actually used commercially. All these cannot be taken up here, but the following type processes may be mentioned: (1) reduction of magnesium compounds by a metal, *e.g.*, reduction of anhydrous fused magnesium chloride with sodium, or of magnesium oxide with aluminum; (2) reduction of magnesium oxide by carbon, followed by sublimation and condensation of the metal; (3) reduction by ferrosilicon or related compounds; (4) electrolysis of anhydrous magnesium chloride or a mixture of magnesium chloride and another chloride (sodium or potassium chloride, or both) in the fused condition; (5) electrolysis of magnesium oxide dissolved in a suitable fused bath, *e.g.*, in magnesium fluoride, in a manner similar to the Hall-Héroult aluminum process; (6) electrolysis of aqueous solutions of magnesium salts; (7) electrolysis of magnesium sulphide in a suitable fused bath.

The first process, *i.e.*, reduction of magnesium chloride by sodium, has been used commercially, but it is out of the question for commercial production now, involving as it does the use of electrolytic sodium. The second process, involving carbon reduction, forms the basis of important plants producing about 4 per cent of the United States production[7].[1] The ferrosilicon reduction process is used by the Ford Motor Co. in Michigan, Magnesium Reduction Co., Luckey, Ohio (National Lead subsidiary), the Permanente Metals Corp. in California, and the New England Lime Co. in Connecticut[40], and will be used by the Electro Metallurgical Corp. and the American Metal Co. and is apparently producing about 24 per cent of the United States production[57]. The fourth process, *i.e.*, electrolysis of fused salt mixtures high in anhydrous magnesium chloride, is largely employed at the present time, and this process is used by the Dow Chemical Co. and others to produce about 72 per cent of the United States production[57], by the Chemische Fabrik Greisheim-Elektron, and by the Magnesium Co. in England. The Mathieson Alkali Works plant at Lake Charles, La., and the Union Potash plant at Austin, Tex., will work on electrolytic methods, as

[1] References are to bibliography at the end of the chapter.

will that of the Diamond Alkali Co. at Painesville, Ohio[36]. The fifth process is analogous to the aluminum-reduction process and was developed and employed by the American Magnesium Corp., but apparently is not used at present. The sixth process is technically unsound because of the high electrolytic-solution pressure of the metal ($E_h = +1.55$ volts). The seventh process appears feasible but has not been used commercially.

The earlier methods for the production of magnesium have been described in published papers by Tucker and Jouard[2], Grosvenor[4], Phalen[10], Flusin[14], Allen[18], Boynton and his coworkers[19], Fedotieff[21], Miyake and Butts[28], Harvey[30], and others, and in many patents, *e.g.*, those of Ashcroft, Seward, Backer, and Harvey.

Magnesium Oxide from Sea Water.—The Dow Chemical Co.'s Texas plant was probably the first to use this process. The sea water is treated after sedimentation with hydrated lime made from calcined oyster shells, and the suspension is sent to Dorr thickeners, whence it goes to filters, for the production of a magnesium hydroxide cake. It would appear that a preliminary treatment with calcium hydroxide equivalent to the amount of iron and alumina in the water would be advisable if the magnesium hydroxide is to be used for the production of anhydrous magnesium chloride. It was reported to the author that Montecatini in Italy certainly gave such a preliminary treatment. In the Dow process, the magnesium hydroxide is then dissolved in hydrochloric acid for the production of magnesium chloride.

If the magnesium hydroxide is to be used for the preparation of magnesium oxide to be reduced by ferrosilicon or carbon, the use of dolomitic lime is preferable to the lime from oyster shells as the precipitant, since this gives an additional amount of magnesium hydroxide at a low cost, and the impurities introduced by the dolomite would have no adverse effect on the process (H. H. Chesny process of preparing magnesium hydroxide). For these reductions, the magnesium hydroxide is dried and calcined at 900 to 1100°C.

In the preparation of magnesium oxide from dolomite, it is important to remember that calcium oxide reacts with magnesium chloride to form magnesium oxide and calcium chloride, and that calcium is precipitated by sodium carbonate in the presence of magnesium chloride without precipitating the magnesium.

Carbon Reduction Process.—This process, usually known as the Hansgirg process, has been described by Paul D. V. Manning[44] and by T. A. Dungan[58]. It was developed in Austria several years ago by Franz Hansgirg, and a small plant was operated until an explosion destroyed the enterprise. A similar installation, on a larger scale, was made first in England by two of Dr. Hansgirg's associates and later in Korea by Dr. Hansgirg himself. In 1941, the Permanente Metals Co. at Permanente, near Los Altos, Calif., built, under the supervision of Dr. Hansgirg, a plant for the production of magnesium metal, which utilized a modification of the original process. (This plant is sometimes referred to in the literature of the metal as the Todd-California Shipbuilding plant.)

Magnesium oxide, produced as pure as possible, is mixed with carbon such as a petroleum coke. This mixture, made into briquettes with a hydrocarbon binder, is then charged continuously into an electric furnace, the magnesium oxide reacting with carbon to produce carbon monoxide and magnesium metal. The reaction is reversible, *i.e.*, the reaction tends to reverse so that carbon monoxide and magnesium produce magnesium oxide and carbon. The reaction goes in favor of producing magnesium metal at a temperature above 2000°C. Magnesium boils under atmospheric pressure at 1107°C. The equilibrium point of the reaction is reached at atmospheric pressure and stoichiometric proportions at about 1850°C. The essential point in this process is, therefore, the removal of the magnesium before it can react

with the carbon monoxide to form carbon and magnesium oxide, the process being carried on at about 2200°C.

In the original Hansgirg plant, built in Austria in 1929, this was accomplished by mixing the magnesium vapor and carbon monoxide, as it left the electric furnace, with a large quantity of refrigerated hydrogen gas. This accomplished what is termed "shock cooling" of the vapor, and the magnesium metal condensed as an impalpable powder. Some impurities were carried over with the vapor, and since the melting of a metallic powder of this fineness is extremely difficult, the next step was to form the powder into small briquettes or pellets and charge them into a retort, from which the metal was distilled under a high vacuum, to be condensed as pure crystallized magnesium.

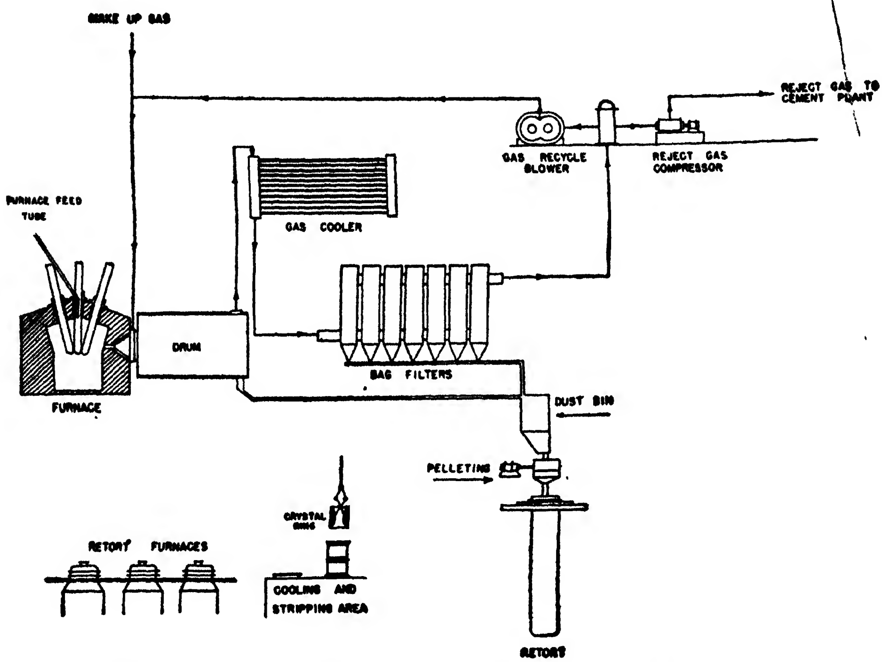


FIG. 1.—Flow sheet, Carbothermic process. (*Courtesy of A.I.M.E.*)

The reaction at Permanente is carried on in a graphite crucible which at its thinnest part (the junction with the roof) is 4 in. thick. The roof is composed of keyed carbon blocks 18 in. thick. The crucible is surrounded by an average thickness of about 4 ft. of fine gas carbon for insulation, and the entire assembly is inside a pressure-tight steel shell 16 ft. in diameter and 16 ft. high[58].

The electrodes are 20 in. in diameter, of machined graphite, and they enter through three holes in the roof 120 deg. apart, and each electrode is on an angle of 11 deg. with the vertical. The stuffing boxes through which these electrodes enter the crucible represent one of the greatest engineering problems in connection with the process.

The carbon monoxide and magnesium escape from the crucible through a 10 in. diameter hole about 8 in. above the coke bed where they enter the shock-chilling cone, from which the mixture of these gases with the refrigerated natural gas goes through a drum 15 ft. in diameter and 34 ft. long. About 20 per cent of the magnesium settles in this drum, and the remainder goes through bag filters. The amount of refrigerated

gas is so proportioned as to maintain a temperature of not over 250°C. in the drum. Between the drum and bag filters is a heat exchanger which cools the gas to 80°C. to protect the filters. The filter dust contains approximately 50 per cent magnesium, 20 per cent carbon, and 30 per cent MgO.

This dust is mixed with an asphalt residue in cleaning solvent or kerosene, and the paste is extruded into the sublimation retorts, where the solvent is first distilled and the asphalt coked to form a nondusting mixture.

The sublimation retorts are vertical cylindrical vessels 56 in. in diameter by 22 ft. high. The upper 8 ft. is the condenser, and there is a heat dam between the sublimation and the condensing portion of the retort. The sublimation is performed under a pressure of about 3 mm. of mercury at a temperature of about 800°C. The retort is heated by Nichrome resistance heaters, and there must be a vacuum outside the retorts as well as within to prevent the collapse of the retorts during the distillation.

Metallic magnesium resulting from the shock-cooling part of the process is extremely pyrophoric; upon exposure to air, it will instantly catch fire. Therefore, it is necessary to store the powder and handle it under an inert atmosphere such as hydrogen or methane. The handling of the vapor and of this highly inflammable magnesium powder are the sources of the principal hazards and troubles that have dogged this process since its development. Numerous fires have occurred in plants using the process, and the Austrian plant finally blew up and was completely destroyed, as before indicated. In the modification of the Hansgirg process in use at Permanente, shock cooling is not accomplished by the use of refrigerated hydrogen but by natural gas. After the removal of the magnesium dust from the resulting mixture of natural gas and carbon monoxide from the cooler, it passes into cement kilns where it is used as a fuel.

Considerable difficulty has been experienced in this process, owing primarily to the necessity of working under gastight conditions and also because of the high temperatures required in operation[44].

Important work on the carbon reduction of magnesia has also been done by H. A. Doerner. His experiments with a small-scale plant are detailed in *Chemical and Metallurgical Engineering*, August, 1942.

The cycle of cooling gas purification, if hydrogen is used, is ingenious, but unfortunately the details cannot be published.

Carbide and Allied Reduction Processes.—Apart from the direct reduction of magnesium oxide by carbon, magnesium oxide can also be reduced by calcium carbide, silicon carbide, silicon, aluminum, and various silicides, such as those of calcium, aluminum, and iron. At least experimentally, the reduction with calcium carbide and with calcium silicide have been carried on in Italy and Germany.

However, they are all of minor importance, except for the ferrosilicon reduction (Pidgeon process) and the use of finely divided aluminum of poor quality to produce first-class magnesium.

The magnesium reduction with calcium carbide is said to be most advantageously carried on as a two-stage process. The magnesium oxide is mixed with an excess of calcium carbide over that necessary to effect reduction and the mixture heated for some time at 1050 to 1150°C. The residue from this operation is mixed with additional magnesium oxide up to the theoretical quantity and there redistilled to produce additional metal.

Ferrosilicon Process.—Practice of the ferrosilicon reduction process as carried out by the Ford Motor Co. has been described by Paul D. V. Manning[44]. Dolomite is calcined to produce "dolime" and is ground to a powder with crushed 75 per cent ferrosilicon mixed with a binder. The proportion of dolomite to ferrosilicon is between five and six parts to one. The mixture is then briquetted.

Finished briquettes are charged into horizontal retorts, 10 in. in diameter and 22 ft. long, made of chrome-nickel steel, set in multiple in a furnace. After charging each retort, the condenser cover is put in place. A high-vacuum pump is started to maintain the charge in the retort under as high a vacuum as possible, and the heat is turned on around the retort. This heat causes the reaction to take place between the ferrosilicon and the calcined dolomite. Magnesium vapor is liberated and is deposited on a condenser head which extends into the end of the retort and which is cooled by water passing through its inner chamber. The magnesium metal is deposited on sleeves at the end of the retort. Approximately eight hours is required for the completion of the reaction, and about 70 lb. of magnesium per retort should result.

According to the National Research Co. of Boston, it is possible to operate large retorts on pressures as low as 0.001 to 0.025 mm. of mercury.

Contaminated aluminum scrap can be used to good advantage in this process, after powdering it, to replace the powdered ferrosilicon in part, and there seems to be no reason why the complete substitution of powdered or granulated aluminum for the ferrosilicon could not be carried out. British patents 405097 and 487836 cover the reduction of dolomite with silicon or ferrosilicon.

Retorts.—The greatest difficulty in the ferrosilicon process has been with the retorts[61, 62]. Various alloys were tried, of which the best were 35 per cent nickel,

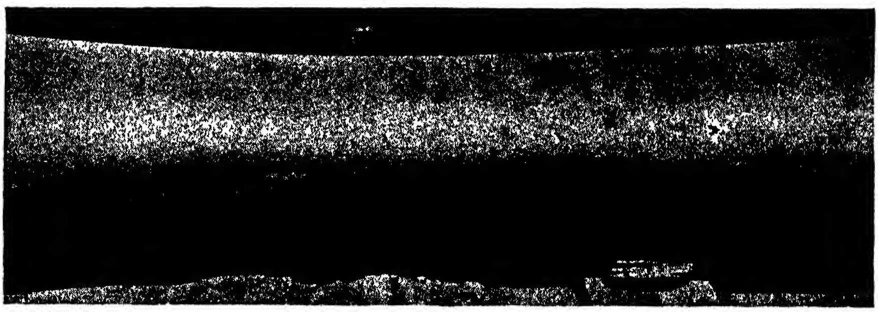


FIG. 2.—Retort after initial collapse. (*Courtesy of Foley and Sebastian*[62].)

15 per cent chromium; 28 per cent chromium, 20 per cent nickel; 28 per cent chromium, 15 per cent nickel; and 25 per cent chromium, 12 per cent nickel. All these seem to stand atmospheric corrosion at the operating temperature (2150°F.), but none was completely satisfactory. In general, the high-chromium alloys were superior to the high nickel.

The first retorts were 10 in. outside diameter and 7/8 in. wall thickness, which was later increased to 1 1/8 in. wall thickness, but even then the retorts collapsed from external pressure. It was found that at the temperature of operation the retorts could be blown up to their original dimensions at an air pressure of about 90 lb. left on for a period of two or more hours. It eventually became the routine procedure to blow the retorts up every 20 days or so. A retort that survived a full year of pilot-plant service had the following composition: C, 0.33 per cent; Mn, 0.89 per cent; Si, 1.61 per cent; Cr, 26.99 per cent; Ni, 15.14 per cent; P, 0.02 per cent; S, 0.022 per cent. The actual results show that a somewhat longer average life appears to result from static casting than from centrifugal casting.

One of the problems of this process which has not yet been solved is the selection of the best and most economical type of retort. For effective reduction, the temperature must be maintained within a narrow range only slightly below the softening

point of the chromium-nickel-steel alloys used in the retorts. The rate of collapse of the tubes in the first plants was higher than expected. The wall thickness of the retorts was increased in early 1943 to 1⅛ in. from ¾ in. and with this change a longer life was attained. As possible substitutes for cast-alloy retorts, two other types are being tried, one with alloy sheet wrapped and welded around a mild steel tube, the other with a layer of chromium-nickel weld metal laid on a similar steel tube. Ford is said to have changed to plain steel retorts immersed in molten glass[40].

The ferrosilicon process is often called the Pidgeon process, after Dr. L. M. Pidgeon. Experimentation with 85 per cent ferrosilicon did not prove to have sufficient additional value to justify its use, and the 75 per cent grade is being used. About 1.1 lb. is used per pound of magnesium produced[35].

FIG. 3.—Full-length view after initial collapse. (*Courtesy of Foley and Sebastian*[62].)

Magnesium Chloride Process.—The older magnesium chloride process for the production of metallic magnesium involves three steps, *viz.*, (1) preparation of anhydrous magnesium chloride as such or in admixture with alkali chlorides; (2) electrolysis of the magnesium chloride in a cell at low voltage; and (3) purification of the resulting metal. In employing hydrous magnesium chloride as the raw material, the water must first be removed, and it should be stated at the outset that the anhydrous salt cannot be produced directly by heating the hydrous material.

When aqueous solutions of magnesium chloride are evaporated and crystallized, the salt obtained is $MgCl_2.6H_2O$. If this salt is heated, it melts in its water of crystallization, and the reaction

$$MgCl_2.6H_2O \rightarrow MgO + 2HCl + 5H_2O$$

takes place, so that the final product is magnesium oxide. The complete dehydration of hydrous magnesium chloride has been made the subject of many patents, and the usual methods employed entail heating the crystallized $MgCl_2.6H_2O$ in admixture with alkali chlorides or in a current of chlorine or hydrochloric acid gas. Thus, in a process of the Dow Chemical Co., the hydrous chloride is first heated[10] at low temperature in admixture with 25 per cent sodium chloride plus a small amount of ammonium chloride, whereby about 50 per cent of the water is driven off. The partly dried mix is then cooled and reheated at higher temperature until the remaining water is removed. In the process of the Magnesium Co., the hydrous chloride is heated[80] for several hours at 150°C. in dry air; part of the water is driven off, yielding a product of the composition 73 per cent $MgCl_2$, 4 per cent MgO, and 23 per cent H_2O. This material is then reheated in a current of hydrochloric acid gas at 300°C., whereby the remaining water is removed, the magnesia converted to magnesium chloride, and a product containing 99+ per cent magnesium chloride obtained. Recovery of chlorine is made in the Dow process and of hydrochloric acid in the process of the Mag-

nesium Co. In all processes devised for the production of anhydrous magnesium chloride, the object in view is to prevent conversion of the chloride to oxide on heating. A process originally developed in Germany and later modified and used in England utilizes the electrolysis of magnesium chloride in a somewhat different way. In this process, it is necessary that the magnesium chloride be absolutely anhydrous, and it is produced by reacting calcined magnesite with carbon monoxide and chlorine to form magnesium chloride and carbon dioxide. In carrying out this process, the calcined magnesite is ground to a fine powder and mixed with lime and magnesium chloride together with fine coal and some peat moss to make the mass porous. The mixture is then briquetted or else pelletized in a rotary kiln and fed into the top of a vertical chlorination furnace. The lower part of each furnace or tower is packed with coke or other carbonaceous material so that when the mass is heated and chlorine is passed in the above reaction takes place. Magnesium chloride runs from the bottom of the furnace as a molten anhydrous liquid. This process is essentially the one that has been installed in Nevada by Basic Magnesium, Inc.[44], controlled by the Anaconda Copper Mining Co.

After preparing anhydrous magnesium chloride or a suitable mixture of this salt with alkali chlorides, the material is electrolyzed at 675 to 725°C. in a suitable cell. Although the decomposition voltage of magnesium chloride is only 3.25 volts, about 5 to 8 volts are required in practice, and the current consumption is 12 to 14 kw.-hr. per lb. of metal produced. In the process, anhydrous magnesium chloride is added to the bath from time to time as electrolysis proceeds in order to keep the bath within the required working limits of composition. Where renewal of the magnesium chloride is not made, a batch process results, and it is preferable to make the operation continuous. Various types of cells are employed. In a single-stage operation the cell is a cylindrical or rectangular iron box having carbon anodes, the iron of the cell serving as the cathode. In some cells, a cathode of steel may be suspended in the bath. The cell is heated externally in starting the process, but after electrolysis begins no further external heating is necessary, since the imposed current serves both for electrolytic dissociation of the salt and for maintaining the temperature of the bath; although it has been rumored that I. G. Farben starts with cold cells, bringing them up to working temperature entirely by the use of electric-current heating. During electrolysis the metal collects at the surface of the cathode in the form of small globules; these gradually grow larger with further deposition of metal and finally detach from the electrode, rising to the surface, where they float. The chlorine is liberated at the anode and is swept out of the cell and recovered. The magnesium is ladled out of the cell from time to time and cast into crude ingots, or is ladled directly into iron pots for purifying. The metal is fluxed in the pots with fused sodium magnesium chloride and cast into ingots or sticks. A small cell taking a 100-lb. charge yields 26 to 28 lb. of metal per 24 hr. Figure 4 shows a form of cell in which a porcelain hood is placed in the bath to keep the floating magnesium from contact with the anodically separated chlorine. In this cell, nitrogen or carbon dioxide is used to sweep out any chlorine that may penetrate to the cathode compartment. The chlorine from the anode is aspirated through the pipe shown and recovered.

The Magnesium Co., of Wolverhampton, England, employed[18] a two-stage process in order to avoid the use of a diaphragm or partitioned cell. The cell was of cast steel with a firebrick lining, fitted with a gastight cover carrying graphite anodes and means for outlet of the chlorine. The cell was charged with liquid lead for the cathode, and this was covered with the electrolyte into which the anodes dip. Means were provided for circulating both the bath and the lead cathode. The cell had a capacity of 5000 amp. at a current density of 1500 amp. per sq. ft. with a voltage drop of 5 at the terminals. The cell was self-heating and produced about 100 lb. of mag-

nesium per 24 hr. as a lead-magnesium alloy, with current efficiency of 85 per cent. The first operation was the electrolysis of the magnesium chloride electrolyte so as to produce a magnesium-lead alloy at the cathode, and in the second stage this alloy acted as the anode in another cell and the cathode consisted of a large number of steel rods immersed in the magnesium chloride electrolyte. The second cell was operated in series with the first at 5000 amp. and a voltage of 2. The total energy consumption was said to have been 8.5 kw.-hr. per lb. of magnesium produced, which seems low. The chlorine was aspirated from the cells to scrubbing towers and absorbed in milk of magnesia with the formation of magnesium chloride and chlorate, with subsequent recovery of the chlorate as $KClO_3$; the magnesium chloride was returned to the process.

Mathieson Alkali and Consolidated Mining & Smelting Co. of Canada are said to have worked out a cell that will operate even if the magnesium chloride contains 20 per cent of water[57], the effluent gas being, it is said, almost pure chlorine.

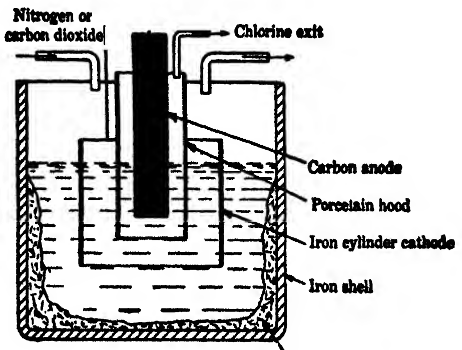


FIG. 4.—Cell for magnesium production from magnesium chloride. (*Rideal.*)

In a patent by Iwahashi and Kishimoto[6], an alternating current of suitable current density is passed into magnesium chloride in a cell using graphite or carbon as anode and iron as cathode; the water in the chloride is evaporated, and the salt said to be fused without decomposition; after the fused salt ceases to bubble, it is electrolyzed by direct current.

Magnesium Oxide Process.—A process for the production of magnesium that is analogous to the Hall-Héroult process for the reduction of aluminum was patented by Seward[7] and by Harvey[8] and was used by the American Magnesium Corp. In this process, substantially pure magnesia, MgO, was dissolved in a liquid (fused) electrolyte, consisting of about equal parts of magnesium fluoride and barium fluoride plus sufficient sodium fluoride to give the required fluidity, and electrolyzed. The magnesia was prepared by the calcination of magnesite obtained from the Pacific coast and shipped to the works at Niagara Falls, N. Y. (In an older patent by Seward and von Kügelgen[9], a process was disclosed for the production of aluminum magnesium alloys by electrolyzing magnesium oxide dissolved in magnesium fluoride plus lithium fluoride, using liquid aluminum as the cathode.) The magnesium-oxide process is discussed by Harvey[30].

The cell or furnace used in the magnesium oxide process may be conveniently described by reference to Figs. 5 and 6. The former shows a transverse section of the furnace, and the latter is a plan. In the figures, 1 is a wrought-iron vessel supported

on blocks 2, and 3 represents the solidified portion of the bath 4. The cathodes are represented by 5, which consist of iron or steel castings extending longitudinally through the furnace and projecting through apertures 6 in the bottom. A layer of asbestos 20 is placed between the cathodes and the furnace shell. The anodes are shown at 9, and these are of graphite or carbon, suspended in the bath. A layer of

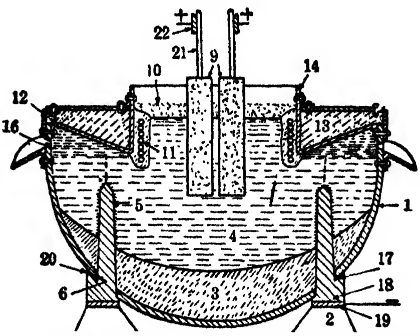


FIG. 5.—Magnesium reduction furnace. (*Seward.*)

magnesium oxide 10 is maintained on top of the bath as a source of raw material. Cooling pipes 11 are arranged between the cathodes and anodes so as to cause solidification of a portion of the bath to form vertical partitions of insulating material. Hoods or collecting chambers are shown at 12 receiving the liquid magnesium which ascends from the cathodes; these chambers are made of cast or sheet-metal casings 13 placed near the surface of the bath and suitably cooled. They are shown as supported

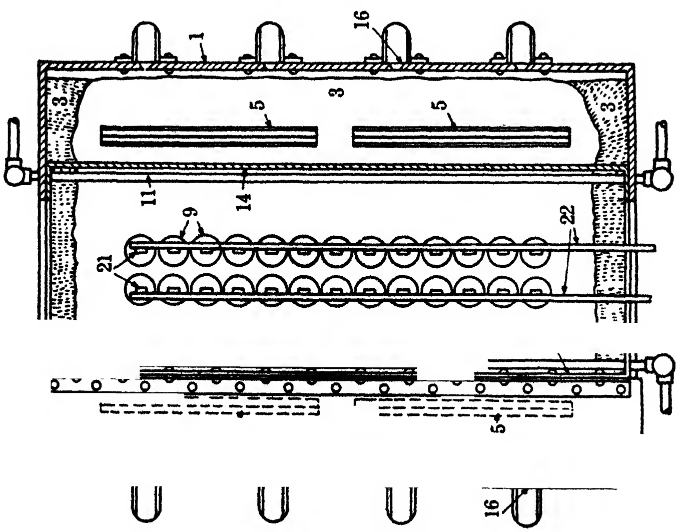


FIG. 6.—Plan of magnesium reduction furnace. (*Seward.*)

from the upper edges of the side walls of the furnace shell 1. The inner wall 14 of each hood is situated sufficiently close to the cooling pipes 11 so that the mass of solidified salts extends to the wall 14 and seals the space between the wall and the pipes. The liquid metal collected in the hoods or chambers may be drawn off continuously or tapped intermittently from tapholes 16. The cathodes 5 are formed with shoulders

17 for receiving the weight of the furnace, and have flat bottoms 18 which rest on flat copper bus bars 19. The anodes are carried by rods 21 and fastened to bus bars 22. In operation of the process, the bath is maintained at about 950°C. and its specific gravity at about 3.2. The magnesium oxide is added to the bath around the anodes at frequent intervals. The current may be 9000 to 13,000 amp. at an e.m.f. of 9 to 16 volts. The average current efficiency may be taken as 50 per cent with a power efficiency of 40 per cent. The dissociated oxygen burns at the carbon anodes; the magnesium is liberated at the cathodes and rises into the collecting chambers from which it is removed. The metal was refined by remelting with a flux, and specially pure metal was prepared by volatilizing the crude magnesium and condensing it.[1]

Magnesium oxide is only slightly soluble in the fluoride bath—in which respect it differs considerably from aluminum oxide—the solubility being only about 0.1 per cent. Strictly speaking, therefore, the process is probably not a direct electrolysis of the oxide. It has been suggested that the mechanism is as follows:

$$MgF_2 = Mg + F_2$$
$$MgO + F_2 = MgF_2 + O$$
$$C + O = CO$$

Commercial Forms of Magnesium.—Substantially pure magnesium is supplied to the trade in the form of sticks, ingots, blocks, rods, bars, tubes, sheets, plate, extrusions, wire, powder, foil, and ribbon. Powder is made 40 to 200 mesh, depending upon requirements. For deoxidizing, the metal is furnished as sticks or in the form of extruded ingot with diameter of about 1¼ in. Flashlight powder usually runs 100 to 150 mesh, while powder for signal lights in marine and military work is usually 50 mesh. Sheet and plate are available in almost any thickness, while rod is produced from ⅜ to 1¼ in. Tubing is made up to 1¼ in. outside diameter, and wire is furnished from No. 36 to No. 00 B. & S. gauge. Ribbon is usually made ⅛ in. wide by 0.006 in. thick. Sand and permanent-mold castings are made in both magnesium and its light alloys.

The Nicol process for the production of magnesium powder is to atomize the molten metal by a high-velocity stream of nitrogen. Table 4, page 60, gives a number of the commonest alloys, as well as the specifications for Grades A, B, and C.

Chemical Properties of Magnesium.—The impurities in magnesium may be divided into two classes, *viz.*, metallic and nonmetallic. The former include aluminum, barium, calcium, copper, iron, silicon, sodium, and potassium. The nonmetallic impurities are usually salts of magnesium such as the oxide and chloride, and chlorides of calcium, potassium, and sodium, as well as occluded bath material and carbon. The bulk of the nonmetallic impurities may be eliminated by a remelting operation.

Pure magnesium (99.99+ per cent) is a silvery-white metal. It consists of three isotopes of masses 24, 25, and 26, in the relative amounts of 7:1:1, yielding a mean atomic weight of 24.336, as compared with the chemical value of 24.32. Magnesium is a basic element and forms salts with mineral and many organic acids. The metal does not oxidize in dry air, but when exposed to moist air it loses its silvery luster and becomes coated with a film of the oxide and possibly carbonate (and hydroxide).

[1] One of the problems of this process is to produce a pure magnesium oxide, since the electrolyte will be contaminated by the progressive building up of any impurities in the added MgO. C. E. Dolbear claims a cyclic process for the production of the pure oxide, based on (1) boiling impure magnesium oxide with ammonium sulphate, the magnesia going into solution; (2) passing the liberated ammonia into cold pure magnesium sulphate solution.

$$MgO + (NH_4)_2SO_4 + aq. = MgSO_4 + 2NH_3 + aq. \text{ (hot)}$$
$$MgSO_4 + 2NH_3 + aq. = Mg(OH)_2 + (NH_4)_2SO_4 + aq. \text{ (cold)}$$

The reaction is said to be applicable to magnesium carbonate also.

Magnesium reduces most oxides, liberating the corresponding metal or nonmetal. Magnesium has a high heat of combustion, the heat of formation of magnesium oxide, MgO, being about 146,000 cal. per gram-atom. The molecular heat of formation of Al_2O_3 is about 386,000 cal., or about 128,700 cal. per gram-atom. The explosibility of magnesium dusts is high, being about 114 as compared with 100 for standard Pittsburgh coal dust. The metal (particularly in powder or ribbon form) burns easily in air and with an intense white light, very rich in actinic rays. This property makes magnesium valuable in photographic work for flashlights. The spectrum of burning magnesium more nearly resembles that of the sun than any other element. Magnesium does not burn directly in the air to oxide, but is converted first to the nitride, which then burns to the oxide. The reaction is accompanied by a faint yellow glow, followed by the peculiar incandescence and white light. Massive magnesium does not readily burn in air except at temperatures far above the melting point.

Dilute acids dissolve the metal rapidly, with violent evolution of hydrogen. Caustic alkali solutions have no action, but hot aqueous solutions of ammonium salts attack it. Strong sulphuric acid acts slowly on magnesium, and mixed acid (sulphuric plus nitric) has slow action at the ordinary temperature. At 20°C. water does not attack the metal, but at 100°C. water is slowly decomposed with the formation of magnesium oxide and hydrogen. The action on hot water is thought to be due to galvanic action between the metal and the impurity iron therein. Magnesium unites with nitrogen below the melting point to form magnesium nitride, Mg_3N_2, and phosphorus reacts with it to form the phosphide (Mg_3P_2). With boron it forms the boride (Mg_3B_2), and it reacts with carbon to form the carbides (MgC_2 and Mg_2C_3). The metal reacts with hydrocarbon gases to form these carbides, setting free hydrogen. It does not react with hydrogen but can be distilled in an atmosphere of this gas. In general, magnesium resists the attack of alkalies and hydrofluoric acid, but is attacked by saline solutions and most acids[30]. One use of potential importance after the war is the possibility of using the metal on a large scale to synthesize organomagnesium halides, such reagents being known as "Grignard's reagents."

Corrosion.—The information given above as to the action of chemical reagents on magnesium is suggestive in determining the corrodibility of the metal and its alloys. Magnesium and its alloys are more corrodible than aluminum and aluminum alloys when exposed to the ordinary corrosive agents. But substantially pure magnesium and light alloys made from such metal exhibit adequate corrosion resistance to ordinary air; they are attacked by solutions of acid salts, neutral solutions of acid salts, and especially by halogen salts. Gasoline, kerosene, and lubricating oils have no action. Solutions of cellulose esters dissolve the metal. Both the metal and its alloys can be protected from ordinary atmospheric and other mild corrosives by painting with lacquers, varnishes, and paints, and by special coatings. Thus, treatment in a bath of sodium bichromate, copper nitrate, and nitric acid causes formation of a colored oxidized layer, probably some copper compound, that protects against atmospheric corrosion. Backer[11] has patented a coating process in which a strongly adherent coating of magnesium hydroxide, $Mg(OH)_2$, is put on by heating the metal or its alloys in water or steam to temperatures above 100°C. for 15 min. under ordinary or raised pressures. The corrosion of magnesium by water can be inhibited by the presence of a small percentage of potassium dichromate in the water. W. S. Loose has patented the use of solutions of hydrofluoric acid, hydrofluosilicic acid, boric acid, and acid and neutral fluorides, followed by treatment with an arsenic compound (assigned to Dow Chemical Co.)[45].

Physical and Mechanical Properties of Magnesium.—Magnesium is the lightest metal used for structural purposes, having a specific gravity of 1.74. The metal weighs 109 lb. per cu. ft. The specific gravity in the liquid state (at 673°C.) is 1.56,

and the solidification shrinkage is 4.2 per cent. The low value 1.74 for the specific gravity makes an equal volume of magnesium weigh about two-thirds as much as aluminum. Magnesium is slightly malleable when cold but very malleable and ductile at 350 to 450°C. The metal and certain alloys can be cast readily in iron molds and dry-sand molds and also worked into shapes. Both magnesium and its light alloys machine easily and take a fine finish. When heated *in vacuo*, magnesium sublimes and deposits in crystals. Table 2 gives a summary of the physical and mechanical properties of magnesium; the figures may be compared with the corresponding properties for aluminum in the chapter on the Metallurgy of Aluminum and Aluminum

TABLE 2.—PHYSICAL, MECHANICAL, AND OTHER PROPERTIES OF MAGNESIUM[1]

Property	Units for expression	Value
Specific gravity, 20°C	Grams per cubic centimeter	1.7388
Specific gravity, liquid, 673°C	Grams per cubic centimeter	1.562
Melting point	Degrees Centigrade	651
Boiling point	Degrees Centigrade	1120
Thermal expansivity	Increase in length per unit of length per degree Centigrade (0 to 100°C.)	0.0000259
Thermal conductivity	Gram-calories per centimeter cube per degree centigrade per second (c. g. s. units).	0.350
Latent heat of fusion	Gram-calories per gram	70
Latent heat of vaporization	Gram-calories per gram	1,700
Specific heat	Gram-calories per degree Centigrade (20 to 100°C.)	0.249
Specific electrical resistance	Microhms per centimeter cubed, at 20°C.	4.46
Temperature coefficient of resistivity	Per degree Centigrade (20°C.)	0.0040
Magnetic susceptibility	$H \times 10^6$, at 18°C.	+0.55
Hardness (cast)	Brinell (10 mm., 500 kg., 30 sec.)	30
Hardness (cast)	Scleroscope:	
	Magnifier hammer	20
	Universal hammer	12
Tensile strength (cast)	Pounds per square inch	13,000
Yield point (cast)	Pounds per square inch	3,000
Elongation (cast)	Per cent	6
Reduction in area (cast)	Per cent	6
Compressive strength (cast)	Pounds per square inch	32,000
Transverse strength (cast)	Pounds per square inch	32,000
Heat of combustion to MgO	Calories per gram-atom	146,000
Heat of chlorination to $MgCl_2$	Calories per gram-molecule	152,000
Heat of sulphuration to MgS	Calories per gram-atom	80,000
Electrolytic solution potential against calomel electrode	Volts	2.82
Atomic weight	O = 16	24.32

[1] Data collected from various sources.

Alloys in this work. Magnesium is a good bearing metal. The mechanical properties of some magnesium alloys are discussed below under Alloys. Magnesium has low proportional limit and ductility, which features preclude its use for some purposes. Moore[29] gives some tests on the mechanical properties of the metal and one alloy.

Magnesium Alloys.—Magnesium-rich alloys are the lightest known useful alloys for engineering construction, their specific gravity falling in the range 1.75 to 1.90, roughly. Their tensile strength lies in the range 20,000 to 50,000 lb. per sq. in., depending upon the alloy and the condition, *i.e.*, whether cast or worked. Magnesium forms alloys with most metals, and the commercial alloys are represented by certain magnesium-zinc, magnesium-aluminum, magnesium-cadmium, magnesium-aluminum-zinc, magnesium-aluminum-cadmium-copper, magnesium-aluminum-zinc-manganese, and other alloys. Magnesium-zinc alloys are represented by the so-called "Elektron metal" of the Chemische Fabrik Griesheim-Elektron, while magnesium-aluminum alloys are made by the Dow Chemical Co. under the name Dowmetal. Substantially pure magnesium and an alloy of the nominal composition 99.5:0.5 magnesium-zinc have been marketed under the name "cork metal."

Some tests have been reported by Beckinsale[15] on the properties of German Elektron metal of the nominal composition 94.5:5:0.5 magnesium-zinc-copper.

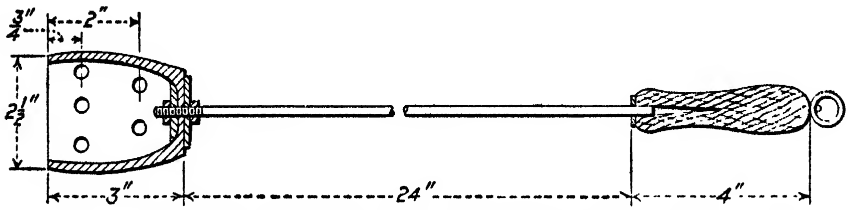


FIG. 7.—Perforated crucible for adding magnesium to alloys. (*Rosenhain.*)

The properties of three samples in the form of cylindrical rods were as follows: specific gravity, 1.78 to 1.79; Brinell hardness (1-mm. ball, 10 kg.), 48 to 63; yield point, 17,000 to 26,900 lb. per sq. in.; tensile strength, 36,100 to 41,200 lb. per sq. in.; elongation, 13 to 19 per cent; specific tenacity, 250 to 284; yield point in compression, 6700 to 18,800 lb. per sq. in.; and compressive strength, 50,000 to 53,500 lb. per sq. in.

About twenty years ago, 87:13 magnesium-copper alloy was employed considerably for pistons in Germany, while the 90:10 magnesium-copper alloy was used somewhat. The 90:10 magnesium-aluminum, 88:12 magnesium-aluminum, and the 90:8:1:1 magnesium-aluminum-copper-cadmium alloys have all been chill-cast for pistons, while the 89:10:1 magnesium-aluminum-silicon alloy has been used for piston-bin bushings. The 87:13 magnesium-copper alloy, sand-cast, has a tensile strength of about 20,000 lb. per sq. in., 1.5 per cent elongation, and 55 Brinell hardness number. Other alloys that have been employed include the 90:5:5 magnesium-aluminum-zinc alloy (for aircraft castings) and the 99:1 magnesium-silicon alloy (for pistons). Certain of the magnesium-base alloys are heat-treatable, *e.g.*, magnesium-aluminum. The heat-treatment of such alloys, as in the case of aluminum alloys, depends on the retention in solid solution of a soluble constituent by quenching and its subsequent precipitation in finely dispersed particles by aging. Thus, a heat-treatable magnesium-aluminum alloy may be quenched from 425°C. and aged at 200°C. to cause precipitation of the Mg_3Al_2. Certain intermediate alloys, *e.g.*, 50:50 and 20:80 magnesium-copper, have been used for deoxidizing in nonferrous practice, and the 69:31 aluminum-magnesium alloy has been employed for mirrors under the name "mirror metal."

In general, the magnesium-aluminum-zinc alloys are far superior to the magnesium-aluminum alloys. As the zinc may run from ½ to 3 per cent, and the aluminum from 6 to 10 per cent, the scrap problem is greatly complicated if several alloys are in simultaneous production, and this has apparently militated against their use in the United States.

Alloys of Mg 91½ : Al 8 : Zn ½ and Mg 90 : Al 9½ : Zn ½ are superior for founding practice. Alloys with 6 Al and ½ Zn or with 2 per cent Mn are good extruding alloys; the 8 Al, ½ Zn is very poor for this use. While the manganese alloys are superior in corrosion resistance, they are below the aluminum-magnesium alloys in strength.

The usual nomenclature and general properties of the alloys currently used in the United States are given in Tables 3 and 4.

The H alloy (American 4) is apparently a favorite German alloy. It is tough, but inclined to porosity. The Germans also use 3 Al : 1 Zn; 4 Al, 3 Zn; 8½ Al : ½ Zn; and 9½ Al : ½ Zn.

The alloy of magnesium with 8½ Al : 3½ Zn is said to give an ultimate tensile strength of 15 to 18 tons per sq. in. after heat-treatment.

As a matter of fact, all magnesium castings should be heat-treated for about 6 hr. at 840°F., and a protective gas must be used in the oven. About ½ to 1 per cent sulphur dioxide in the furnace atmosphere gives the castings ample protection. The

TABLE 3.—MAGNESIUM ALLOY SPECIFICATION EQUIVALENTS[1]

Type	Basic Magnesium, Inc., alloy	A.S.T.M.		Navy Bureau Aeronautics		Army Air Corps specification	Dow Chemical Co. Dowmetal alloy	American Magnesium Corp. alloy
		Alloy No.	Specification	Alloy No.	Specification			
Casting:								
Sand casting.......	BMI-4	4	B-80-41T[b]	4	M-112	57.74-10	H	AM-265
	BMI-11	11	B-80-41T[b]	11	M-112	......	M	AM-403
	BMI-17	17	B-80-41T[b]	17	M-112	......	C	AM-260
	BMI-A8[a]							
	BMI-AZ91[a]							
Die casting.........	BMI-13	13	B-94-40T[b]	..	M-369	11319	R	AM-263
	BMI-A8[a]							
	BMI-AZ91[b]							
Permanent mold....	BMI-A8[a]							
	BMI-AZ91[a]							
Wrought:								
Extrusions.........	BMI-AZ855[a]	9	B-107-41T					
	BMI-8	8	B-107-41T	8	M-126	11320	J	AM-57-S
	BMI-11	11	B-107-41T	11	M-126	11320	M	AM-3-S
Forgings...........	BMI-AZ85[a]	9	B-91-41T					
	BMI-8	8	B-91-41T	..	.....	......	J	AM-57-S
	BMI-9	9	B-91-41T	..	.....	11321	O	AM-58-S
Sheet..............	BMI-8	8	B-90-41T					
	BMI-11	11	B-90-41T	11	M-111	11317	M	AM-3-S

[1] Courtesy Basic Magnesium, Inc.

[a] These alloys are similar to the English and German alloys of these numbers.

[b] These specifications are for the castings themselves. The ingot specifications are B-93-41T.

TABLE 4.—MAGNESIUM ALLOYS IN COMMON USE

Alloy	Dow metal	Use	Allowable impurities									
			Al	Tn	Mn, min.	Si, max.	Cu, max.	Fe, max.	Ni, max.	Pb, max.	Total other, max.	Strength as cast, tons per sq. in.
2	G	SC	9.4–10.6	....	0.13	0.02	0.01	0.02	0.001	0.001	0.20	8.9
B93-41T		SC	9 4–10.6	......	0.13	0.20	0.04	....	0.020	.....	0.30	
4[a]	H	SC	5.5– 6.5	2 7–3.3	0.18–0.50	0.02	0.01	....	0.001	0.001	0.10	12.1
B93-41T[b]		SC	5.5– 6.5	2.7–3.3	0.18	0 20	0.04	....	0.020	.....	0.30	
Grade A[c]		SC	5.3– 6.7	2.5–3.5	0.15	0.30	0.05	....	0.010	.....	0.30	
8[d, e]	J	EFS	5 8– 7.2	0 5–1 5	0.17	0.02	0.01	0.02	0.001	0.001	0.10	18.7
B90-41T[d]		S	5 8– 7 2	0 4–1 5	0.15	0.30	0.05	....	0.030	.....	0.30	
B91-41T[d]		F	5 8– 7.2	0 4–1 5	0.15	0.30	0.05	0.02	0.030	0.001	0.30	11.6
B107-41T[d]		E	5.8– 7.2	0.4–1.5	0.15	0.30	00.5	0.02	0.030	0.001	0.30	
9		F	7.8– 9.2	0.2–0.8	0.15	0.30	0.05	....	0.030	.....	0.30	
B107-41T		F										
B91-41T		F										
11 321	O	F	8.0–10.0	0.50	....	....	....	....	.....	.....	....	13.4
11	M	SC	....	... ...	1.3	0.01	0.01	....	0.001	.....	0.20	
11[d]	M	ES	....	....	1 3	0.01	0.01	....	0.001	0.001	0.20	
B93-41T[b]		SC	....	....	1 2	0.10	0.04	....	0.020	.....	0.20	
B90-41T		S	....	....	1.2	0.30	0.05	....	0.030	.....	0.30	
B107-41T		E	....	....	1.2	0.30	0.05	....	0.030	.....	0.30	
Grade B[c]		SC	....	....	1.2	0.30	0.05	....	0.010	.....	0.20	
13[b, f]	R	D	8.5– 9.5	0.5–0.9	0.15	0.02	0.01	0.02	0.001	0.001	0.10	
B-94-40T		D	8.3– 9.7	0.4–1.0	0.13	0.05	0.05	....	0.030	.....	0.30	
Grade 1[g]		D	8.0–11.0	1.0 max.	0.10	1.0	0.05	....	0.030	.....	0.30	
17[i]	C	SC, PM	8 5– 9.5	1.7–2.3	0.13	0.02	0.01	0.02	0.001	0.001	0.10	10.3
B91-41T		SC, PM	8.5– 9.5	1 7–2.3	0.13	0.20	0.04	....	0.020	.....	0.30	
Grade C[c]		SC	8.3– 9 7	1.7–2.3	0.10	0.30	0.05	....	0.010	.....	0.30	

TABLE 4.—MAGNESIUM ALLOYS IN COMMON USE.—(Continued)

Alloy	Dow metal	Use	Allowable impurities									
			Al	Tn	Mn, min.	Si, max.	Cu, max.	Fe, max.	Ni, max.	Pb, max.	Total other, max.	Strength as cast, tons per sq. in.
18[d]	....	EFS	2.4– 3.0	0.8–1.3	0.22	0.02	0.01	0.02	0.001	0.001	0.20	
B90-41T[d]	....	S	2.4– 3.0	0.7–1.3	0.20	0.30	0.05	....	0.030	.....	0.30	
B91-41T[d]	....	F	2.4– 3.0	0.7–1.3	0.20	0.03	0.05	....	0.030	.....	0.30	
B107-41T[d]	....	E	2 4– 3.0	0.7–1 3	0.20	0.30	0.05	....	0.030	.....	0.30	
A8[h]	....	....	7.6– 8.5	3.5 max.	0.5 max.	0.10	0.02	0.02	0.002	.....	0.30	
A231												
AZ285												
AZ855	....	....	7.8– 9.2	0.2–0.8	0.15	0.30	0.05	....	0.03	.....	0.30	
AZ91	....	....	7.5– 8.5	0.4–0.55	0.15–0.25							
AZG	....	....	9.5–10.5	0.4–1.0	0.5 max.	0.10	0.02	0.02	0.002	.....	0.30	
	....	....	6.0	3.5	0.5							
	DTD-59A	SC	8 5	3.5	....	0.4	0.4	0.01	.....	0.4		
	DTD-88B	F	6.0– 8.0	0.5								
	DTD-289	....	8.5	0.5	....	....	....	....	.....	.....	1.0	
	DTD-142	....	....	....	2.0	....	....	....	.....	.....	....	8.0

NOTES: SC, sand casting; PM, permanent mold casting; D, die casting; E, extrusion; F, forging; S, sheet, strip or plate.

[a] 4X—Fe, 0.003; Ni, 0.0036.

[b] Ingot specifications for casting.

[c] Grades A, B, and C are defined by Specifications AN-QQ-M56, a fabricated product specification.

[d] Finished product specifications.

[e] 8X—Fe, 0.005; Ni, 0.005.

[f] 13X—Fe, 0.003; Ni, 0.003.

[g] Grade 1 is defined by A.A.F. specifications 11319.

[h] A8X—Fe, 0.005.

[i] 17X—Fe, 0.003; Ni, 0.003.

treatment for 6 hr. at 840°F. may be considered a minimum. E. F. Cone recommends 12 hr. at 715 to 730°F. for solution and 16 hr. additional at 350°F. for aging[56].

Magnesium is a constituent of certain aluminum alloys, *e.g.*, duralumin, zinc duralumin, magnaliums, and so-called Y-alloy of the National Physical Laboratory (92.5:4:1.5:2 aluminum-copper-magnesium-nickel). Magnesium is present in duralumin and zinc duralumin in an amount of 0.5 to 1.0 per cent, and by the formation of magnesium silicide, Mg_2Si, is largely responsible for the duralumin phenomenon. Magnalumins are aluminum-rich alloys containing magnesium up to 10 per cent and magnesium with other elements.

Melting and Casting.—Magnesium alloys are more difficult to prepare than are aluminum alloys. In practice, the magnesium is usually melted in cast iron or steel pots fired by oil or gas and the alloys with aluminum and with zinc are made simply by adding definite amounts of solid metals to liquid magnesium. Manganese is preferably added by using a flux that contains manganese chloride, the manganese being reduced by the magnesium. The Dow Chemical Co. has two such fluxes; its No. 250 (melting) consists of 23KCl, $72MgCl_2$, $2\frac{1}{2}BaCl_2$, and $2\frac{1}{2}CaF_2$. This flux is usually used following a refining with the Dow No. 230 flux, which is a general open-pot flux consisting of 55KCl, $34MgCl_2$, $9BaCl_2$, and $2CaF_2$. The Dow Chemical Co.'s No. 320 is another flux used for the introduction of manganese. This contains $76MnCl_2$, $13CaF_2$, and 11MgO. This is used after a refining with No. 310 flux, which consists of 20KCl, $50MgCl_2$, $15CaF_2$, and 15MgO.

The British refining fluxes used where we use the Dow 320 and 230 are $MgCl_2$, 30; NaCl, 30; KCl, 30; and MgF_2, 10, or less commonly $MgCl_2$, 39; $CaCl_2$, 15; NaCl, 7; KCl, 7; CaF_2, 20; MgO, 12.

A flux recommended by Dow Chemical for refining metal in a covered pot provided with SO_2 surface protection is No. 220, 57KCl, $28CaCl_2$, $12\frac{1}{2}BaCl_2$, and $2\frac{1}{2}CaF_2$. This flux is removed after refining. A British flux used for melting is $MgCl_2$, 33; $CaCl_2$, 30; NaCl, 15; KCl, 15; and MgO, 1.

There are various other fluxes on the market that appear to be mixtures of the various chlorides and fluorides already mentioned, and some appear to contain borates and boric acid and sulphur. Schreiber and Beck[17] patented the use of sulphur as a flux, the idea being to cause a layer of sulphur vapor to float above the liquid metal, while above that was a layer of sulphur dioxide from the combustion of this vapor. Veazey and Burdick[12] and Gann[13] held patents for various halide mixes, but these patents have now expired. Oxidation on melting has been discussed by de Fleury[31] in a paper that is still a classic.

The older workers recommended that magnesium or its alloys should not be heated to a temperature exceeding 1350°F., but it appears that a superheating (say 15 min.) at 1650 to 1750°F. refines the grain of aluminum alloy. However, if this is given, it is important that the metal be brought down to pouring temperature and poured with little delay. The grain refinement is rapidly lost on standing at pouring temperatures (say around 1450°F.)

Magnesium cannot be poured into green sand (water-tempered) molds since it reacts with the moisture. For green-sand molds with magnesium, the usual water is replaced with kerosene, glycerine, or ethylene glycol, which prevents ignition of the hot metal. A sand of 1G to 2G grade should be used.[1] An exception to the above is in the use of synthetic sands [such a mixture is silica sand (minus 40 mesh), 91 per cent; boric acid, ½ per cent; sulphur, 4½ per cent; bentonite, 4 per cent]. This mixture has been successfully employed, using about 3½ per cent of water for mixing. Cores may be bonded with dextrin, corn oil, or sodium silicate solution and baked.

[1] The American Foundrymen's Association is using the following classification for foundry sand. Clay content is denoted by letter:

The synthetic sand mentioned above may be used for cores, but in this case the sand is a little coarser than 40 mesh, and a little less sulphur is used. Some authorities recommend a dusting of the mold with bentonite or graphite. The sand for magnesium-alloy casting should be permeable and the molds freely vented. Magnesium cannot be poured directly into molds; some device such as a pouring cup must be used to break the fall of the metal, so as to reduce the amount of air carried into the mold as greatly as possible. A current of nitrogen or chlorine gas flowing through the molds is sometimes recommended to reduce the porosity of the castings, but does not appear to be necessary. Gates and risers of great size must be used; in fact, the gates and risers may weigh two and one-half to three times what the casting does from which they are cut off[64].

Precipitation of Iron.—There is a tendency for iron to be introduced into magnesium alloys through the magnesium itself, from the iron pickup in remelting magnesium scrap, from the aluminum, from the flux, and from the crucible itself. If manganese is introduced by the use of manganese chloride or the Dow 250 or 320 flux, spoken of above, to the saturation point during the superheating to produce grain refining, the iron is precipitated to the bottom of the crucible on reducing to the pouring temperature. The iron contents may be reduced to 0.001 per cent by this process. Any attempt to remelt or reheat such high-purity alloys appreciably above 1300 to 1350°F. in steel crucibles will inevitably lead to recontamination by iron.

A sand— 0 up to but not including 0.5 per cent clay
B sand— 0.5 and up to but not including 2.0 per cent clay
C sand— 2.0 and up to but not including 5.0 per cent clay
D sand— 5.0 and up to but not including 10.0 per cent clay
E sand—10.0 and up to but not including 15.0 per cent clay
F sand—15.0 and up to but not including 20.0 per cent clay
G sand—20.0 and up to but not including 30.0 per cent clay
H sand—30.0 and up to but not including 45.0 per cent clay

The fineness is then expressed by a series of arbitrary numbers, derived as follows: The sand, freed from clay, is screened, and the residues on the screens expressed as per cents are multiplied by the following factors:

On 6 mesh	× 3
Through 6, on 12 mesh	× 5
Through 12, on 20 mesh	× 10
Through 20, on 30 mesh	× 20
Through 30, on 40 mesh	× 30
Through 40, on 50 mesh	× 40
Through 50, on 70 mesh	× 50
Through 70, on 100 mesh	× 70
Through 100, on 140 mesh	× 100
Through 140, on 200 mesh	× 140
Through 200, on 270-mesh	× 200
Through 270 mesh	× 300

The products of these multiplications are then added and divided by the total percentage of sand, *i.e.*, the clay is excluded. The sand is then classified according to the quotient thus obtained.

No. 1 sand corresponds to quotients from 200–300
No. 2 sand corresponds to quotients from 140–199
No. 3 sand corresponds to quotients from 100–139
No. 4 sand corresponds to quotients from 70– 99
No. 5 sand corresponds to quotients from 50– 69
No. 6 sand corresponds to quotients from 40– 49
No. 7 sand corresponds to quotients from 30– 39
No. 8 sand corresponds to quotients from 20– 29
No. 9 sand corresponds to quotients from 10– 19

From "Standards and Tentative Standards for Testing and Grading Foundry Sands," American Foundrymen's Association, July, 1938.

As indicated previously, magnesium is used to a considerable extent as a deoxidizer in nonferrous foundry practice. It is also a minor alloying element or a constituent in subordinate amount in certain alloys. For making fixed additions of magnesium, it is advisable not to add the entire amount at once by simply throwing the metal into a liquid melt, but small pieces may be pushed under the surface by tongs and held until dissolved. If thrown into a liquid melt, the magnesium will break up, float on the surface, and burn. A useful device for making fixed additions of magnesium is a form of "phosphorizer," such as is used in adding phosphorus to alloys. The tubular device of Naylor and Hutton (U.S. patent 1475055) is useful, or the perforated crucible [16] shown in Fig. 7 may be employed.

Impregnation of Magnesium Castings.—Even with the utmost care, there is a decided tendency for magnesium castings to be porous. This tendency can be corrected to some extent by impregnating the castings with tung oil or with sodium silicate solution under pressure. In the case of sodium silicate, the casting has to be thoroughly cleaned, or unsightly stains result. Tung oil seems to be the better reagent, though it has been difficult and sometimes impossible to get under war conditions. Pressures up to 200 lb. per sq. in. and temperature up to 475°F. are often used. This, of course, necessitates carrying the process on in an autoclave.

Anodizing.—Consolidated Vultee Aircraft Corporation has recently announced that it has a corrosion- and abrasion-resisting finish, produced by anodizing in an alkaline solution, which will apparently be made generally available to industry. Except that it requires a fairly close temperature control (from 171 to 179°F.), no details have been given out.

Mechanical Treatment.—Both magnesium and certain magnesium-rich alloys can be readily rolled hot and to some extent cold, but when rolled cold frequent annealings are necessary between passes in order to avoid cracking. Both the metal and magnesium-base alloys containing, for example, up to 10 per cent aluminum or zinc are worked (rolled or forged) at 350 to 400°C., and extruded at 550°C. The ordinary ribbon is made by pressing the semifluid metal into wire and then flattening it. The powder is made by disintegrating the metal in the pasty condition, or by milling. Magnesium and its alloys are soldered with great difficulty, but welding is done similar to aluminum welding. The use of a slightly reducing oxyacetylene flame and fluoride fluxes is recommended. Both magnesium and magnesium alloys may be machined very rapidly and easily, and the machinability of magnesium is unexceeded by any other metal. It exhibits no dragging tendency as does aluminum, and all machine-tool operations can be carried out much faster than on aluminum and its alloys. Welding is also carried on, using a hollow electrode through which helium is passed to give a neutral atmosphere.

Metallography.—Magnesium has a hexagonal close-packed lattice, with lattice parameter $a = 3.22$ and $c = 5.23$ (axial ratio 1.624). Magnesium does not work well because of its crystal structure. The ductile and malleable metals (like aluminum) have face-centered cubic lattices. The constitution and metallography of many binary systems of magnesium with other metals have been examined, and the diagrams of thermal equilibrium published [25]. Magnesium and its alloys may be etched satisfactorily with dilute acids, *e.g.*, acetic acid and nitric acid. A solution of 1 per cent hydrochloric acid plus 0.5 per cent nitric acid in alcohol is also a satisfactory etching reagent.

Selected Bibliography.—The literature on magnesium in general, particularly the chemical side, is large. A few of the more important references are given below.

1. LEJEAL, A.: "L'aluminium, le baryum, le strontium, le calcium, le manganèse, et le magnésium," J. B. Ballière et fils, Paris, 1894.

BERYLLIUM[1]

Sources.—From a commercial standpoint, the only beryllium mineral now warranting attention is beryl, $3BeO.Al_2O_3.6SiO_2$, which is of fairly widespread occurrence. The chief deposits are in Brazil, Argentina, India, Canada, and Portugal. When pure this contains about 14 per cent beryllium oxide. The mineral richest in beryllium is phenacite, $(BeO)_2SiO_2$, or beryllium orthosilicate, which contains 45.55 per cent beryllium oxide when pure. If anyone is ever fortunate enough to discover a large deposit of it, it will revolutionize beryllium metallurgy.

Gadolinite, $2BeO.FeO.2Y_2O_3.2SiO_2$, is often referred to as a beryllium mineral, though the occurrences are comparatively scant and it is of more interest as a source of yttrium than it is of beryllium.

There has been a good deal of talk recently regarding some occurrences of helvite occurring in the United States. Helvite is a complex manganese-iron beryllium silicate, and apart from difficulties that would arise in its treatment because of its composition, the beryllium content of the known deposits is not high.

Early Metallurgy.—The element beryllium was first isolated by L. N. Vauquelin in 1797.[2] He crushed and heated beryl, having the idea that this heating made the mineral more readily amenable to attack by chemicals, and then mixed the mineral with three times its weight of caustic potash and fused the mixture. The melt after cooling was dissolved in hydrochloric acid, dehydrated, and again taken up with hydrochloric acid and filtered to separate the silica. The filtrate was treated with an excess of potassium carbonate, and the precipitate after draining was leached with a solution of caustic potash which dissolved the alumina. The undissolved material was, in Vauquelin's own words, *une terre nouvelle.* He dissolved this precipitate with nitric acid and evaporated to dryness, took up with hydrochloric acid and threw the iron out with potassium hydrosulphide, though he found that to make a complete separation of the iron involved a second treatment. The solution after throwing out the iron had a pronounced sweet taste, and though Vauquelin always speaks of working on *terre du béril* he suggests that the new element should be known as "glucine" (glucinum) from the Greek word for sweet, because of this outstanding property.

Vauquelin did considerable work on the comparison of aluminum and beryllium, working out a separation of most of the aluminum based on its precipitation as alum.

[1] An abridgement of this section, by the editor, appears in the Non-ferrous Metallurgy volume of the American Institute of Mining and Metallurgical Engineers.

[2] *Ann. chim. phys.*, Vol. 26. pp. 115–179. 1798.

His work is reviewed at some length, since ordinarily his procedure is incorrectly set forth in modern metallurgical works. It will also be recognized by those who have studied beryllium metallurgy that a good many technicians have followed his ideas since, including preheating the beryl before treatment, which has even been allowed as an invention in recent patent claims. The fusion with caustic alkali has been done by H. N. Warren (1894), G. Wyrouboff (1902), J. H. Pollok (1903), C. L. Parsons and Barnes (1906), F. Bran and G. Van Ordt (1907), L. Petit-Devaucelle (1926), and C. F. Brush, H. Fischer, H. H. Armstrong, G. Jaeger, and C. Adamoli, to cite only those processes immediately occurring to the author. R. H. McKee worked with alkalies in solution in an autoclave, rather than by fusion.

Vauquelin also proved the existence in the emerald of the same new element that he had found in beryl.

Humphrey Davy (about 1808) and Wöhler (1827) produced an impure metallic beryllium by reducing the oxide with metallic sodium or metallic potassium.

The first use of alkaline carbonates as decomposition agents came over half a century later. Henri Debray in 1854 pulverized beryl and fused it with half its weight of calcium oxide.[1] The mass obtained by this fusion he powdered and treated with dilute nitric acid until a homogeneous jelly was produced. Then he evaporated the jelly to dryness and calcined until the nitrates of beryllium and iron were decomposed as well as some of the calcium nitrate. This residue he treated with ammonium chloride. Apparently he counted on the evolution of ammonia by the decomposed calcium nitrate to keep most of the iron and alumina in the insoluble residue with the silica. If there was no evolution of ammonia, he argued that he had not carried his calcination far enough. He filtered off the solution of beryllium and calcium and poured the filtrate into an excess of ammoniacal ammonium carbonate solution and allowed the mixture to stand for 7 or 8 days, and then added some ammonium hydrosulphide to precipitate the iron completely. He then filtered off the pure beryllium solution, which he concentrated by boiling until basic beryllium carbonate separated as a white powder. Again, metallurgists who have worked with beryllium will recognize that Debray's caustic lime decomposition of beryl has formed the basis for at least a dozen metallurgical processes based on this method of attack.

Debray refers at some length to Berthier's work on the separation of beryllium from alumina. Berthier suspended the well-washed mixture of these earths in water and passed in sulphur dioxide until they dissolved, after which he boiled off the excess of sulphur dioxide. Berthier claimed that the alumina precipitated and left the beryllium in solution. Debray thinks it is an inferior separation, although it still figures in some modern patent work.

The first decomposition of beryl with fluorine that the author has found was that of G. Sheffer in 1858, who heated beryl with fluorspar and sulphuric acid, thus driving off the silicon as silicon tetrafluoride.[2] The excess hydrofluoric acid is also driven off. He leached the residue with dilute sulphuric acid and threw out most of the alumina as an ammonium or sodium alum. The rest of the alumina was thrown out by treating the solution with zinc, which produced an insoluble basic aluminum carbonate. The zinc which had dissolved then had to be in turn removed in part as potassium zinc sulphate and finally as zinc sulphide, the beryllium eventually being precipitated by the use of ammonium carbonate.

John Gibson in 1893 decomposed beryl with ammonium fluoride. This will also be recognized as a precursor of various recent patents. P. Lebeau as early as 1895 described a process based on fusing beryl with twice its weight of calcium fluoride, which he stated could be done at a comparatively moderate temperature. He

[1] *Ann. chim. phys.*, Vol. 54, 3d series, pp. 5–41, 1855.
[2] *Ann. Chem. Pharm.*, Vol. 33, p. 144–147, 1859.

treated the melt with sulphuric acid, driving off silicon tetrafluoride and hydrofluoric acid.

Lebeau also treated beryl in an electric furnace with an excess of carbon, reducing some of the silica to silicon, which distilled off, and in part reducing it to silicon carbide and ferrosilicon. The aluminum and beryllium were converted into carbides. This electric-furnace product disintegrates by weathering and is easily attacked by sulphuric acid.

In 1915, H. Copaux took out French patent 476475 which is based on fusing beryl with sodium fluosilicate. This process, sometimes with the addition of alkaline hydroxides or carbonates or of sodium fluoride, has since been followed by a number of inventors.

Electric-furnace Processes.—Other metallurgists also worked with the electric furnace. L. Burgess produced beryllium carbide or beryllium silicide in an electric furnace, distilling off beryllium chloride. He also reduced under such conditions as to form tetraberyllium trisilicide and also worked on a method for concentrating beryllium in a scoria by forming ferrosilicon in the furnace, using an insufficient amount of carbon to reduce the beryllium (U.S. patent 1905340 of 1933).

B. R. F. Kjillgren also worked on this idea of the production of ferrosilicon (U.S. patent 2092621 of 1937).

H. Lowenstein based his process on the production of beryllium sulphide, using pyrite as a source of his sulphur and thus sulphurizing the beryllium (U.S. patent 1777267 of 1930).

D. Gardner worked on the production of beryllium sulphide by sulphurizing with carbon disulphide in the presence of an excess of carbon at 1800 to 2000°C. (U.S. patent 2166659 of 1930).

H. H. Armstrong reduced with carbon or CaC_2 at a temperature high enough to volatilize the Si, then leached with H_2SO_4 (U.S. patent 2273168 of 1943).

Reduction to Metal.—Although certain early experimenters following the procedure of Davy and Wöhler claimed to have produced beryllium 99.8 per cent pure, it seems probable that Lebeau was the first to prepare metal of this or higher purity, which he did in 1894 by electrolyzing Na_2BeF_4 at a temperature below red heat, using a nickel crucible to contain the electrolyte. This crucible also served as his cathode. The anode was graphite.

One of the great obstacles to recovering beryllium as the pure metal is its extreme lightness. The slags or scorias produced by chemical reduction are often heavier than the metal so that the metal floats on top of them instead of being protected by them. In the electrolytic production of beryllium, the fused electrolyte is often heavier than the metal, which means that it is difficult to prevent the metal from taking fire at the anode. This lightness of the metal is one of the reasons why it is easier to produce a master alloy of beryllium rather than the pure metal.

Commercial Processes.—In general, modern processes for beryllium production are based on bringing beryllium into solution as an alkaline fluoberyllate as initiated by Copaux or as beryllium sulphate or chloride, usually, in the last-named methods, dissolving the beryllium after a preliminary decomposition of the beryl by an alkaline hydroxide or carbonate or an alkaline-earth oxide or carbonate. High-temperature chlorination has also been resorted to for the direct production of chloride, using chlorine, hydrochloric acid, and carbon tetrachloride or various combinations of them.

The fluoride-recovery processes take various forms, as the fusion with sodium fluosilicate as devised by Copaux spoken of above, or by attack by hydrofluoric acid at high temperatures, or silicon tetrafluoride at high temperatures, or in organic solution; by treatment with ammonium fluoride both as a gas or in solution under pressure; by the use of acid sodium fluoride either under pressure or at high tempera-

ture; and most recent of all by the Kawecki process (U.S. patent 2312297 of 1943) employing sodium iron fluoride (iron cryolite).

All these processes depend on the fact that the alkaline fluoberyllates are soluble in water though beryllium fluoride is not.

As stated above, sulphate solutions are usually prepared after decomposition of the beryl with the alkaline or alkaline-earth hydroxides or carbonates, though Sawyer (U.S. patent 1823864) in 1931 claimed the use of sulphuric acid on the beryl itself after heating to 1000°C. Jaeger and Wille in 1939 (U.S. patent 2160547) claimed that beryl could be decomposed by treatment with sulphuric acid or acid sulphate if a small amount of fluoride was present, stating that only one-tenth of the amount of the costly fluorine radical was necessary in this process that would be required for a complete decomposition of the beryl with fluorine.

One inventor rather dodges his responsibilities by stating that he prepares a sulphate solution "in any well-known manner."

Reduction to Metal.—There is no outstanding method for the reduction of beryllium metal any more than there is any process for the decomposition of beryl that is comparatively unequaled. There are various patents and processes covering the electrolysis of beryllium fluoride or beryllium oxyfluoride, $BeO.5BeF_2$, such as those of Cooper, Zeppelin, Fischer, and Adamoli; for the electrolysis of beryllium fluoride in solution in molten calcium fluoride and in various halide electrolytes, and for the electrolysis of beryllium chloride in electrolytes where the metallic base of the solvent is more electropositive than is beryllium, such as sodium, potassium, or lithium chloride or mixtures of them. The electrolysis of beryllium hydroxide or beryllium chloride in solution in anhydrous ammonia has also been patented by Booth, Torrey, and Merlub-Sobel (U.S. patent 1893221). The use of sodium or potassium to reduce beryllium halides over 100 years ago by various experimenters has already been commented on. Magnesium has also been used to reduce the normal sodium fluoberyllate, Na_2BeF_4, the monosodium fluoberyllate, $NaBeF_3$, and also beryllium chloride. It may be noted in passing that the reduction of chemically pure Na_2BeF_4 by pure magnesium is likely to result in a disastrous explosion. The direct reduction of beryllium oxide by magnesium fails because of the extreme infusibility of the oxide. The reaction quickly comes to a halt because of the lack of contact between the reducer and the material to be reduced.

Beryllium is like alumium in that reduction by carbon produces a carbide rather than beryllium metal. It likewise resembles aluminum in that the reduction of beryllium and a basic metal for the production of a master alloy can be performed by the use of carbon, which reaction has been patented by Gahagan (2193482) and Gruber and Hessenbruch (2228310). Beryllium can also be produced in the same manner as magnesium by thermal reduction with carbon, the beryllium being volatilized and then condensed. Beryllium can also be reduced by carbon in the presence of hydrogen. Some experimenters have claimed that the hydrogen must be in the atomic form but the writer does not feel sure that this has been proved.

Other properties that make the metallurgy of this element a perplexing problem are the following: the metal has a high fusion point and a high vapor pressure at a temperature of not much above the fusion point; the pure metal is exceedingly light and has a tendency to float on slags and on fused electrolytes; the halides are all highly deliquescent, and after they have absorbed water from the air, they cannot be reconverted to an anhydrous salt by simple heating, as all the halides hydrolize readily; when beryllium hydroxide is precipitated, it has a tendency to occlude and adsorb other salts and there is also a tendency to form basic and oxysalts. In short, beryllium deserves the characterization given it by Dr. C. B. Sawyer, of being "the world's No. 1 metallurgical headache."

Perosa Process.—While it would be possible for anyone to construct his own flow sheet from the information that has already been given, it may be of interest to follow in detail the recovery of the metal by the Perosa process.

The beryl is heated and is then crushed and ground so that 100 per cent passes 100 mesh. It is then mixed with acid sodium fluoride in the proportion of 4 atoms of fluorine to 1 atom of beryllium, and this mixture is briquetted. The beryllium is converted to sodium fluoberyllate when the briquettes are sintered at 650 to 800°C. The sintered briquettes are crushed and ground and leached with hot water. The filtered solution is then purified from iron, manganese, and alumina by being made exactly neutral by the addition of sodium hydroxide, and a little potassium permanganate is added. The iron-manganese-alumina precipitate is filtered off, and an excess of sodium hydroxide added to the solution. Beryllium hydroxide is precipitated, which is filtered off, washed, and dried. The drying temperature should not exceed the decomposition temperature of the hydroxide by more than a few degrees; for if it is dried at too high a temperature, its reactivity becomes less than if it is dried close to its decomposition point. After drying, the material is ground in a paint mill with acid ammonium fluoride, which converts the hydroxide to ammonium beryllium fluoride. The ammonium-beryllium fluoride is then briquetted and heated at a temperature sufficiently high to drive off the ammonium fluoride, leaving pure beryllium fluoride behind. This beryllium fluoride is then reduced with magnesium or a magnesium alloy in the presence of some of the metal of which it is desired to form a master alloy.

Because of the high cost of fluorine, no matter what the form in which it is obtained, the solution from the precipitation of the beryllium hydroxide must be treated to recover fluorine, as must also the slags from the final reduction.

Uses of Beryllium.—Except for alloying purposes, the metal has no great value. The greatest use of beryllium is in the production of alloys with copper. These alloys require proper heat-treatment to bring out their best characteristics, this heat-treatment being covered by U.S. patents 1975112 and 1975113 issued to Masing and Dahl, rights to which are held by the Beryllium Co. of America. When properly heat-treated the alloys, particularly in the range 2.3 to 2.6 beryllium, develop a tensile strength comparable to good steel with a fatigue limit which far exceeds that of many steels. The beryllium-copper alloys, even when the beryllium is in small quantity, have a high resistance to many forms of chemical corrosion.

Some of the beryllium-nickel alloys, particularly those approximating 4 per cent Be, 96 per cent Ni, also have an amazing resistance to corrosion and have fine mechanical properties. It is understood that these alloys have been used to a considerable extent for surgical instruments by the Germans.

The supply of beryllium has been insufficient during the war to meet even the demands for master alloys to make cuproberyllium, nickel-beryllium, and some other alloys for military use. There has been some interesting work done on light alloys of magnesium, aluminum, and beryllium stabilized with at least two other elements and employing fairly high percentages of beryllium (in the neighborhood of 22 to 25 per cent). Whether these alloys will find any commercial use after the war will have to wait until it can be seen what the beryllium supply will be and what will be taken by the low-percentage uses.

Determination of Beryllium.[1]—The ore, usually beryl, should be ground until 100 per cent passes 100 mesh. Fuse 0.5 g. of the ground ore with potassium sodium carbonate in a platinum crucible, for at least 20 min.

[1] Courtesy Lucius Pitkin & Co., New York.

Transfer the melt to a porcelain casserole, and dissolve in HCl. Evaporate to dryness on a water bath, repeating the evaporation with HCl to ensure dehydration of the silica. After the second evaporation, bake in a hot plate.

Filter off the insoluble residue, dry and ignite in a platinum crucible, then treat the residue with HF and H_2SO_4 until the silica is expelled. Fuse the silica-free residue in platinum with $HKSO_4$ and dissolve the melt, filter, and add the filtrate to the main solution.

The solution is made slightly ammoniacal and the excess ammonia boiled off. Filter, redissolve the precipitate in HCl, and reprecipitate with NH_3.

Evaporate the united filtrates to fumes with an excess of sulphuric acid, dissolve in water, filter, and once more treat with ammonia. If there were fluorides in the original sample, more NH_3 precipitate will form. Add it to the main NH_3 precipitate, if it does.

Dissolve the hydroxide precipitate in 5 to 10 cc. of HCl, and dilute the solution to about 400 cc. Make barely ammoniacal, and then make barely acid with HCl.

Then, while stirring, add an excess of hydroxyquinoline solution (5 per cent in 2*N* acetic acid), then 10 cc. of neutral concentrated ammonium-acetate solution. Heat, while stirring, to 60°C., on a water bath and allow to stand. If the precipitate is not too voluminous, it can be filtered on filter paper, otherwise it should be filtered on a gooch with the aid of suction. Wash well with cold water.

The filtrate contains the Be, the precipitate contains the iron and alumina. Add excess NH_3, boil on a hot plate to expel the excess, then filter off the $Be(OH)_2$ on an ashless filter and wash with hot water containing some ammonium acetate and a few drops of NH_3.

Dry in a platinum crucible, incinerate carefully, and heat in a full Bunsen flame to constant weight. The residue is Be. $BeO \times 0.3626 = Be$.

The iron and aluminum can be determined in the hydroquinoline precipitate after destroying the organic matter by a treatment with nitric acid and sulphuric acid.

CHAPTER III

THE ALKALI AND ALKALINE-EARTH METALS

By A. C. Loonam[1]

This chapter deals with eight metals which occupy a peculiar place in metallurgy. Three of them, calcium, sodium, and potassium, are among the five most abundant metals in the earth's crust. Two others, barium and strontium, are plentiful and even the rarest, cesium, is no rarer than such well-known metals as cadmium, mercury, and antimony. Lithium is actually as abundant as zinc, and rubidium is also widely distributed. Their compounds are of great importance in every phase of life, yet the metals themselves are not generally known. Only one of them, sodium, is produced in considerable quantity, but practically all of it goes for use as an industrial chemical and not as a metal.

The reason for this, of course, is that these metals lack the physical properties that make others valuable. They are soft, weak, and rapidly corroded, and are therefore unsuitable for structural purposes. However, they have properties that make them of interest to metallurgists. They are all good conductors of heat and electricity; they form alloys that are liquid at the melting point of ice; their very reactivity makes them valuable as scavengers; their ability to form high melting compounds with some metals has resulted in new methods of metal purification; some of them show definite promise as minor alloy constituents; and last, but by no means least, three of them are becoming very important in the new and rapidly growing field of electronics.

THE ALKALI METALS

The alkali metals, in the order of their economic importance as metals, are sodium, potassium, lithium, cesium, and rubidium. These metals are the most electropositive of all the elements. They are silvery white, soft, and malleable. The hardness decreases in the order Li, Na, K, Rb, Cs. Lithium, the hardest, is softer than lead, while sodium and potassium are readily kneaded in the fingers. All have the same crystal structure, a body-centered cubic lattice.

They are only slightly affected by dry air, but in moist air they quickly become coated with layers of hydroxide and carbonate which are not protective. In the case of lithium, the nitride appears to form first and then is hydrolyzed by the atmospheric moisture. For this reason, they must be kept either in sealed containers or under an inert liquid such as kerosene. When heated in air, they react to form peroxides such as Na_2O_2 and K_2O_4. Lithium is an exception to this in that it forms a mixture of oxide and nitride.

They react vigorously with water, alcohol, and dilute acids at ordinary temperature, with the evolution of hydrogen to produce either the hydroxides or the corresponding salts. These hydroxides are very soluble, strongly alkaline, and very caustic, and are the most stable known in that they can be heated to very high temperatures without dissociation.

The salts of these metals are colorless, except when the acid radical is colored. Most of them are readily soluble in water. The few notable exceptions are the carbonate, phosphate, and fluoride of lithium; the pyroantimoniate and some complex

[1] Consulting metallurgist, Deutsch & Loonam, New York.

uranyl acetates of sodium; the chlorplatinates, acid tartrates, hexanitrocobaltates (cobaltinitrites), and perchlorates of potassium, rubidium, and cesium; and the fluosilicates of all the metals except lithium. Cesium also forms insoluble complex chlorides with stannic, plumbic, and antimonious chlorides which are useful in separating it from the other elements. The aluminum alums of potassium, rubidium, and cesium decrease in solubility in the order named and have also been used for separations.

Two unusual properties of these metals are their ability to form salts with hydrogen (hydrides) and their solubility in liquid ammonia. In the hydrides, of the type LiH, the hydrogen is present as a negative ion, just as the chlorine is in NaCl. When fused and electrolyzed, the hydrogen is evolved at the anode. These substances are decomposed by water, liberating one molecule of hydrogen for each molecule of hydride.

Dilute solutions of these metals in liquid ammonia are blue, transparent, and conduct an electric current electrolytically just as do aqueous salt solutions. Concentrated solutions, on the other hand, have a metallic luster and conduct the current electronically as do the metals.

Most of the salts of these elements impart characteristic colors to the Bunsen flame.

The principal physical properties of these metals are given in Table 1.

TABLE 1.—PHYSICAL PROPERTIES

	Li	Na	K	Rb	Cs
Atomic weight	6.94	23.00	39.10	85.48	132.91
Specific gravity, 20°C.	0.53	0.97	0.86	1.53	1.9
Coefficient of expansion per °C. at room temperature, $\times 10^{-6}$	56	71	83	90	97
Melting point, °C.	186	97.7	63.5	39	28
Boiling point, °C.	1372	892	774	679	690
Heat of fusion, cal. per g	159	27.4	14.7	6.1	3.8
Heat of vaporization, cal. per g	4650	1005	484	212	123
Mean specific heat solid, 0° to melting point, cal. per g	1.046	0.293	.177	0.083	0.054
Liquid	1.08	0.326	.197	0.092	0.060
Gas	0.716	0.216	.127	0.058	0.037
Electrical resistivity,[a] 0°C.	8.55	4.2	6.15	12.5[c]	18.83
Thermal conductivity, c.g.s. units[b]	0.17	0.323	.237		

[a] Microhms per cm. cube.
[b] Cal. per sq. cm. per sec. per cm. per °C.
[c] 20°C.

SODIUM

Sodium is by far the most important, industrially, of all the metals considered in this chapter.

Occurrence.—Sodium is very plentiful. According to F. W. Clarke it is the sixth most abundant element, making up 2.75 per cent of the 10-mile crust of the earth, or lithosphere, and 1.14 per cent of the watery layer, or hydrosphere. It is an important constituent of the rock-forming silicates.

The most important source of sodium and its compounds is common salt, NaCl, the mineral halite. Enormous deposits of this substance occur in different parts of

the world, the most important United States deposits being in the New York-Pennsylvania-Ohio area, in Michigan, along the Gulf Coast of Mississippi, Louisiana, and Texas, in Kansas, and in the western Virginia-West Virginia area.

While some salt is mined by underground methods, the greater part is recovered by drilling wells, admitting water, and pumping the brine out. Considerable quantities of salt are also recovered from sea water by solar evaporation, from salt lakes, and from underground brines.

Other sodium salts, such as the nitrate, sulphate, carbonates, and borate, are also found naturally in economic quantities. Of these, the nitrate and borate are valuable for their acid radicals, while the output of the others is small compared with supplies from other sources.

Metallurgy. 1. *Thermal.*—Although sodium was first prepared by electrolysis by Davy in 1807, this method was to wait for over three-quarters of a century before being placed in commercial use, mainly because of the lack of large supplies of electric current.

Meanwhile, thermal methods were developed. In 1808, Gay-Lussac and Thenard observed that metallic iron would reduce sodium hydroxide at high temperature. In the same year, Curaudau discovered that sodium carbonate could be reduced by charcoal. This process was brought to its highest state of development by H. Sainte-Claire Deville who used the metal in his process for producing aluminum. He heated an intimate mixture of Na_2CO_3, charcoal, and chalk in a horizontal iron retort and condensed the volatilized sodium in a specially designed condenser. This condenser, developed by Donny and Maresca in 1852, presented a large surface for radiation and was a considerable advance over those previously in use. The purpose of the chalk was to prevent the separation of the fused carbonate from the rest of the charge. Later it was found that the addition of iron or its oxide to the charge accelerated the reaction.

Later, H. Y. Castner invented a process in which sodium hydroxide was reduced in iron retorts by highly carburized iron. This apparently was considered an improvement over the Deville process.

Sodium can be liberated from its compounds by other reducing agents. Aluminum, magnesium, and, probably, also calcium and calcium carbide will reduce the hydroxide at high temperatures. Calcium and calcium carbide will react with the chloride. Finally, 75 per cent ferrosilicon will reduce the oxide. This fact has become widely known in the last few years as a result of the use of this reducing agent for the production of magnesium. The sodium present in the calcined dolomite was reduced and volatilized. It condensed at a point nearer the end of the retorts than the magnesium and frequently ignited when the retorts were opened. An outstanding contribution of Dr. L. M. Pidgeon to the success of this process was his development of a condenser in which the sodium was collected separately from the magnesium and therefore had less chance of igniting the latter when it caught fire.

2. *Electrolytic Methods.*—It has not yet been found possible to deposit sodium directly from aqueous solutions of its compounds. The reason for this is the high discharge potential of the metal compared with that of hydrogen. Theoretically, this difference could be overcome by using a solution in which the ratio of concentration of sodium ion to hydrogen ion is sufficiently high or if a high hydrogen overvoltage could be secured at a sodium surface. However, even a saturated sodium hydroxide solution does not give the ion ratio required, and the greatest practical current densities do not give the needed overvoltage.

Sodium can be readily electrolyzed into mercury from aqueous sodium-salt solutions. This is comparatively easy for two reasons: (1) the discharge potential of the sodium is lower because a dilute solution of the metal in mercury is produced,

and not the pure metal, and (2) the hydrogen overvoltage at a mercury surface is high. Thousands of tons of sodium are electrolyzed into mercury from NaCl solutions in alkali-chlorine cells every year only to have the amalgam decomposed by reaction with water to produce caustic soda.

The possibility of recovering the sodium by distillation of the mercury from this amalgam has attracted the attention of inventors for many years, and this interest continues. The chief difficulties apparently have been the large amount of mercury to be distilled per unit of sodium produced, losses of mercury in the process, and the difficulty of removing the last traces of mercury from the sodium. However, the application of modern physicochemical methods may overcome these and make the process commercially feasible. One recent patent,[1] for instance, calls for cooling of the amalgam from the cell to crystallize out a solid phase much richer in sodium, which is removed by filtration and treated further while the impoverished mercury is returned to the cell. Another[2] describes the use of an alkaline-earth metal, such as calcium, to remove the last traces of mercury from the molten alkali metal in a manner similar to the use of zinc in the Parkes process.

At the present time, practically all metallic sodium is produced by the electrolysis of fused salts. A great many ingenious cells have been designed for this purpose, some of them even reaching the stage of commercial operation, but only two, those of Castner and of Downs, have stood the test of time.

The Castner Cell.—The development of direct-current generating machinery during the seventies and eighties of the last century provided the large supplies of cheap electric power required for electrolytic processes. H. Y. Castner patented his cell in 1890. It quickly displaced the thermal processes and reached a dominant position, which it held until about 1924 when the Downs cell appeared. It is now no longer in use in the United States.

The cell, which is shown in Fig. 1, consisted of a cast-iron pot open at the top and with an opening at the bottom to which an iron sleeve was attached. The iron cathode leadin passed up through this sleeve and was held in place and insulated from it by frozen electrolyte. The cathode itself, the enlarged end at the top of the leadin, was also of iron. The anodes were suspended from the cover of the cell, to which the positive lead was attached, and were of iron or nickel; if of iron, the anode and cover were sometimes cast in one piece. Through a hole in the center of the cover, and carefully insulated from it, was suspended another iron sleeve to the bottom of which was attached a cylinder of iron or nickel gauze. This cylinder served as a metal well and had a removable cover to permit removal of metal, while the gauze that hung between the electrodes prevented the sodium from reaching the anode, since its high surface tension and its inability to wet the gauze prevented it from passing through the meshes. The cell cover had openings for feed and for escape of gases.

The electrolyte was fused sodium hydroxide. This material has several advantages: its melting point is low, 318°C., it is not corrosive to iron, and the anode product, oxygen, permits the use of iron or nickel as anode, and requires no elaborate collecting system.

The temperature of operation was kept as low as possible, not more than 10 to 20° above the melting point of the bath, which was lower than that of pure caustic because of the presence of impurities, including water. The reason for this was that the current efficiency fell off rapidly and became small at only slightly higher temperatures. Even at best, the efficiency could have been no better than 50 per cent, as an amount of hydrogen equivalent to that of the sodium was liberated at the cathode. This hydrogen came from decomposition of the water which was produced together

[1] U. S. patent 2224814.

[2] British patent 505112, May 4, 1939.

with oxygen by the discharge of OH^- ion at the anode and carried to the cathode. The solubility of water in NaOH at operating temperatures is considerable. The presence of this hydrogen necessitated the greatest care to prevent its mixing with oxygen and causing explosions. As it was, minor explosions were of frequent occurrence owing to a number of reasons.[1]

During operation the liberated sodium was removed from the metal well by means of a perforated ladle which permitted the fused bath to drain off while retaining the metal. In actual practice, the current efficiency averaged about 40 per cent, while the cell voltage was about 5.0. The energy consumption was therefore about 6.6 kw-hr. per lb. of metal.

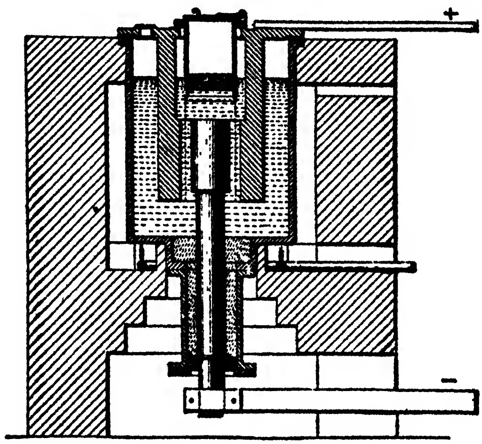


FIG. 1.—Castner cell.

The Downs Cell.—The logical raw material for the production of metallic sodium is common salt. It is cheap and plentiful, chlorine can be recovered as a coproduct, and current efficiencies much greater than 50 per cent should be obtainable. On the other hand, it has a number of disadvantages; its melting point is high (803°C.), a temperature at which the vapor pressure of sodium, which is lighter than salt, is almost half an atmosphere; it rapidly attacks refractories; and the chlorine produced is difficult to handle. Its advantages were early recognized, and numerous attempts were made to overcome the difficulties. Some workers, such as Ashcroft and Carrier, tried to use a divided cell similar to the mercury caustic-chlorine cell. Molten salt was electrolyzed in one compartment with a graphite anode and a molten lead cathode. The chlorine given off at the anode was collected, while the lead-sodium alloy was caused to flow to another compartment containing molten caustic soda. Here it served as an anode with the result that the sodium was electrolyzed out of the alloy and deposited on an iron cathode suspended in the bath. Other workers, including McNitt and Seward and von Kügelgen, attempted to produce the sodium directly.

It remained, however, for J. C. Downs,[2] in 1924, to solve all the difficulties involved. This cell, which is shown in Fig. 2, and which now accounts for by far the greater part of the sodium produced in the United States, must be ranked with the Hall aluminum cell and the Dow magnesium cell as one of the most successful fused electrolytic cells yet developed. It consists of a steel box lined with refractory and insulating brick. The graphite anode extends downward through the bottom of the

[1] ALLMAND and ELLINGHAM, "Applied Electrochemistry," p. 498.
[2] U. S. patent 1501756 (1924).

tank to the electrical connections. The cathode is an iron ring supported on iron leads that extend through the sides of the cell to the electrical connections. Over the anode, and submerged in the electrolyte, is a conical bell which, according to the patent, may be of iron or refractory, for collecting the chlorine. Surrounding the lower edge of the bell is an inverted annular launder, also submerged, for collecting the sodium. Screens attached to the edges of this launder and extending downward on both sides of the cathode serve to prevent the sodium from being carried away. A riser attached to the top of the launder permits the metal to flow continuously into an external sump. The riser extends far enough above the bath level so that the metal, because of its low specific gravity, can overflow but the bath cannot. The riser and sump also permit the metal to cool before it is discharged. An opening in the cell cover is provided for charging.

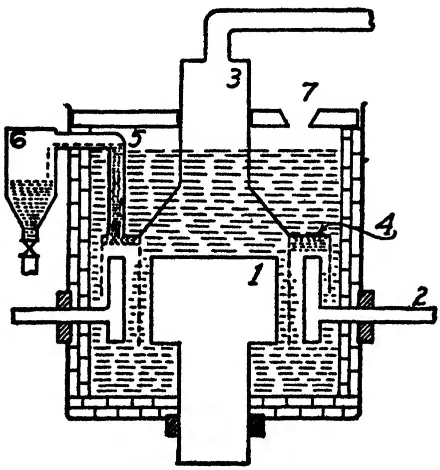


FIG. 2.—The Downs sodium cell. (From Riegel's "Industrial Chemistry," p. 314, *courtesy of Reinhold Publishing Co.*)

The electrolyte is not pure salt but a mixture of this with calcium chloride. These form a eutectic containing 66.8 per cent $CaCl_2$ and melting at 505°C. The use of this mixture, with its lower melting point, permits lower operating temperatures with resulting reduced wear and tear on the cell parts. The actual operating temperature is around 600°C.

The metal deposited at the cathode is not pure sodium but an alloy containing calcium. The amount of calcium in the alloy is not known, but calculations based on the Ca-Na equilibrium diagram and thermodynamic data indicate a concentration of 1.4 per cent if the bath has the eutectic composition. It may be higher than this but cannot exceed about 5.5 per cent, the solubility limit at 600°.

It can be removed by cooling as its solubility decreases rapidly as the temperature is reduced, becoming about 4 per cent at 400°, 2 per cent at 200°, and a very low value at the melting point of sodium, 97.7°C. If the cooling in the riser is considerable, an appreciable amount may crystallize out there and, because of its higher density, fall back into contact with the electrolyte and react with it to reproduce the equilibrium alloy. Other methods can also be used. R. E. Hulse has patented[1] a method in which the calcium containing alloy is brought into contact with solid salt, whereupon the calcium forms calcium chloride and sodium. Finally, the method, mentioned above, of using calcium to remove mercury from sodium can probably be turned

[1] U. S. patent 2224820.

around; *i.e.*, mercury can be used to remove calcium. In any case, the purity of the metal marketed leaves little to be desired as it is considerably better than 99.9 per cent.

The chlorine produced by the cell is pure enough to be liquefied.

The salt is very carefully purified and heated to a high temperature to remove all possible water before being fed to the cell. In spite of this, some water gets in and causes minor explosions during operation.

The current efficiency of the cell is high, probably better than 85 per cent. Mantell[1] gives the voltage as about 7. These correspond to an energy consumption of 4.4 kw.-hr. per lb. of metal.

The sodium is cast into 1-, 2½-, and 12-lb. ingots or "bricks" which are packed in removable head drums holding 280 lb. or in cases of 50 and 100 lb. Larger quantities are shipped in tank cars similar to those used for sulphuric acid and other industrial chemicals. The cars, made by the American Car & Foundry Co., and possibly by other manufacturers, hold 40 tons each. The molten metal is pumped into them, allowed to freeze, and remelted before unloading. This is probably the only case in which a metal has been shipped in such a manner. The low melting point, low specific gravity, and fairly large-scale production and use make this possible.

Production and Prices.—According to T. P. Hou,[2] there were two plants producing sodium in the United States, one at Niagara Falls, N. Y., and the other at Baton Rouge, La., with a total capacity of 120 tons a day as of the end of 1940. The world production for 1941 was estimated at 300,000 tons.[3]

The present published price is 15½ cents per lb., f.o.b. Niagara Falls, for untrimmed bricks.

Uses.—The present important uses for sodium are based entirely on its chemical properties. Large quantities are made into a lead-sodium alloy for the manufacture of tetraethyl lead for high-octane gasoline. The alloy reacts with ethyl chloride in accordance with the equation

$$Na_4Pb + 4C_2H_5Cl = (C_2H_5)_4Pb + 4NaCl$$

An important product, from a metallurgical standpoint, is sodium cyanide. When the metal is heated in ammonia, it forms sodamide, and this, when treated with charcoal, yields sodium cyanide. This high-grade product is used in electroplating and in heat-treatment of metals.

When heated in excess air or oxygen, sodium does not form the normal oxide but goes over to the peroxide, Na_2O_2, a light yellowish-white powder. This substance is really a salt of hydrogen peroxide and is therefore a powerful oxidizing agent. It is manufactured on a large scale and is widely used as a bleaching agent and for the manufacture of other oxidizing agents such as sodium perborate.

Sodium is also an essential raw material in the manufacture of a number of important organic compounds.

Of interest to metallurgists is the fact that a small amount of sodium (0.05 per cent) added to aluminum-silicon casting alloys shifts the eutectic composition from the normal value of 11.7 per cent silicon to 14 per cent. The eutectic temperature is also lowered from 577 to 564°C. By this treatment the microstructure of an alloy with 13 per cent Si, which would normally contain brittle primary crystals of silicon in a ground mass of Al-Si eutectic, is transformed into one with primary crystals of aluminum in a ground mass of extremely fine eutectic with a resultant improvement in physical properties, notably in tensile strength and elongation. According to

[1] "Industrial Electrochemistry."

[2] "Manufacture of Soda," 2d ed., p. 320.

[3] *Mineral Ind.*, Vol. 50, p. 611.

Edwards, Frary, and Jeffries,[1] the optimum concentration of sodium in the alloy is 0.014 per cent, but an excess must be added to allow for losses.

Sodium is an excellent conductor of electricity. On a volume basis its conductivity is about 36 per cent of that of copper, but on a weight basis it is about 3.3 times as good. Some years ago the Dow Chemical Co. built an outdoor conductor of sodium-filled steel pipe, with a capacity of 4000 amp. direct current. An article[2] was published describing the installation, and it was stated that no appreciable increase in resistance was noted after 10 months' service.

Addition of sodium to the mercury used in the amalgamation of gold ores sometimes improves recovery. This was also recommended at one time for platinum ores. The sodium increases the ability of the mercury to wet the precious metals. This same property is the basis of a recommendation that small amounts of sodium be added to metals used for hot-dip coatings.

The metal has been recommended as a heat-transfer medium because of its low melting point, high boiling point, and excellent thermal conductivity. It is completely inert in iron and steel in the absence of air and moisture. An interesting use in this connection is in airplane-engine valves. These are made hollow and are partially filled with sodium, which aids in keeping them cool by greatly increasing the heat transfer from the head to the stem and thus to the lubricant.

Another use for the metal is the removal of arsenic and antimony from lead-tin alloys. However, anyone using this process should remember that the dross formed will contain sodium arsenide which reacts readily with moisture, even that in the air, to form arsine, an extremely poisonous gas.

A very important application, although it accounts for only a small consumption of the metal, is the sodium-vapor lamp now widely used for highway lighting. In this lamp an electric current is passed through sodium vapor at low pressure, causing it to emit the well-known D lines of the sodium spectrum. These lines account for a large fraction of the energy supplied and lie in the region of the spectrum to which the human eye is most sensitive. The lamp is therefore very efficient.

POTASSIUM

This metal is much less important commercially than sodium.

Occurrence.—Potassium is the seventh most abundant element in the earth's crust according to F. W. Clarke, who states that it accounts for 2.58 per cent of the lithosphere and 0.04 per cent of the hydrosphere. These figures show an important difference between this metal and sodium in that, although it is almost as abundant in the solid crust of the earth as the other, it is much less so in the waters, principally, of course, the oceans. This tendency of potassium to remain in or return to the solid phase has the important consequence that large deposits of soluble salts of this metal occur much less frequently than those of sodium. However, rare though they are, they are the chief commercial sources of the metal and its compounds.

The principal deposits of potassium salts are at Stassfurt, Germany, in Alsace, France, and in the area around Carlsbad, New Mexico. Other sources that have produced commercial quantities are the nitrate beds in Chile which contain appreciable quantities and from which a nitrate high in potassium has been produced, underground brines at Salduro, Utah, Searles Lake in California, and the Dead Sea in Palestine, the waters of which are high in potassium salts and constitute the richest source in the British Empire. During the First World War considerable quantities were recovered from cement plants. The potassium in the rock was volatilized in the kilns and recovered in Cottrell precipitators.

[1] "The Aluminum Industry," Vol. II, pp. 72–75, 209–215.

[2] *Trans. Electrochem. Soc.*, Vol. 62, p. 151, 1932.

The discovery of the Carlsbad deposits during the 1920's was of extreme importance to the United States. It provided this country with its own supply of this important fertilizer and avoided the situation that occurred during the First World War when our supply from Germany was cut off.

In the Stassfurt deposits, the potassium occurs as a number of complex salts from which it is recovered by leaching and fractional crystallization. The working out of this process represents one of the first and one of the greatest triumphs of modern physical chemistry and the application of the phase rule.

The Carlsbad deposits consist mainly of a mixture of sylvite, KCl, and halite, NaCl, although one mine contains a commercial deposit of langbeinite, $K_2SO_4.2MgSO_4$. The two chlorides are separated by flotation in saturated brine. There are two processes in use; in one the halite is floated away from the sylvite, while in the other it is the sylvite that floats.

Metallurgy. 1. *Thermal.*—Potassium can be prepared by any of the methods used for sodium. Reduction by carbon, however, is complicated by the fact that, unlike sodium, metallic potassium tends to combine with carbon monoxide to form a highly explosive compound of the formula $K_2C_2O_2$. The metal vapor must be condensed and the liquid metal cooled rapidly to a low temperature to avoid its formation. Rubidium and cesium act similarly to potassium.

The dolomite supply of one of the magnesium plants using the Pidgeon process during the Second World War contained potassium as well as sodium. Both were reduced by the ferrosilicon with the result that a liquid Na-K alloy was condensed which could be tapped from the retorts by opening a valve. Consideration was given to recovering the potassium from this alloy by fractional distillation but, so far as is known, no actual production came from this source.

The principal producer of sodium for general industrial use in the United States is making a commercial grade of potassium by treating one of its salts, presumably the chloride, with sodium. It would be difficult and expensive to prepare metal substantially free from sodium by this process, but the crude product should be entirely suitable for most commercial purposes.

2. *Electrolytic.*—As in the case of sodium, potassium has not yet been deposited directly from aqueous solutions, but, also similarly to sodium, it can be electrolyzed into a mercury cathode. This could be the basis of a process for the recovery of this metal just as for the other but, judging from the patent literature, the interest has been much less than in the commercially more important sodium.

The metal can be produced by electrolysis of its fused hydroxide. The Castner sodium cell, however, is not suitable for this purpose as it does not provide sufficient protection of the metal from the air since potassium is much more reactive with oxygen than sodium. On the other hand, as von Hevesy[1] showed, if suitable precautions are taken, higher current efficiencies can be secured with this metal than with the other, as its solubility in its hydroxide is less and its rate of diffusion lower. He used a cathode surrounded by a magnesia crucible to protect the metal from the air. O. P. Watts[2] describes a laboratory experiment for making potassium which is based on von Hevesy's work. He recommends thrusting an iron wire cathode through the bottom of a magnesium oxide crucible and inverting this in the fused KOH. A piece of sheet iron is used as an anode. There are explosions when the current is first turned on owing to reaction of the potassium with the air in the crucible. The author states that a current efficiency of about 58 per cent has been obtained with this arrangement.

[1] *Z. Elektrochem.*, Vol. 15, p. 539, 1909.
[2] "A Laboratory Course in Electrochemistry."

The production of potassium by electrolysis of its fused chloride presents a number of difficulties, one of which is the fact that its boiling point is about the same as the melting point of the chloride (774°C.). Because of the strongly electropositive nature of the metal, there are relatively few salts that could be added to the bath to reduce its melting point without fear of contamination. Potassium fluoride, which forms a eutectic with the chloride having a melting point of 605°C., appears to be the most promising, with barium chloride (melting point of eutectic 660°) a possibility and potassium bromide suitable for laboratory work. A. Matthiessen claimed, in 1855, that he obtained potassium free from calcium by electrolyzing an "equimolecular" mixture of potassium and calcium chlorides, but there is some reason to doubt this. Although his mixture probably contained 66⅔ molecular per cent KCl (calcium was considered to have a valence of one at that time), Moldenhauer and Anderson[1] recovered a product that was chiefly calcium from a bath containing 69 molecular per cent KCl, although there was evidence that some potassium was formed.

Linneman produced the metal by the electrolysis of fused potassium cyanide.

Production, Prices, and Use.—There is no information available regarding production and prices. The metal has no large-scale application. Its high equivalent weight and high price compared with sodium discourage its use even where its greater reactivity would cause it to be preferred. Increased availability may, however, change this situation.

One important use, which, however, accounts for only a minor consumption, is that in photoelectric cells. The photosensitivity of potassium extends into the visible region of the spectrum and is superior to that of sodium in this respect and, although inferior to cesium and rubidium, the metal is much more plentiful.

Sodium and potassium form alloys that are liquid at ordinary temperatures. That with the lowest melting point, −12.5°C., has the composition 22.7 per cent sodium and 77.3 per cent potassium. These alloys have been suggested for use in high-temperature thermometers.

LITHIUM

Lithium is the lightest of all the metals. Although it is definitely a member of the alkali group, it resembles the alkaline earths in some of its properties, such as the low solubilities of its carbonate, fluoride, and phosphate and its formation of a stable carbide and silicide.

Occurrence.—Although generally considered a rare element, lithium is really as abundant in the earth's crust as zinc and more so than such common metals as lead, tin, cadmium, and antimony. However, it is widely distributed, and there are comparatively few workable deposits.

Spodumene, $LiAl(SiO_3)_2$, and the lithia micas, lepidolite and zinnwaldite, are economically the most important lithium minerals. Spodumene, which contains about 3 to 8 per cent Li_2O, is the chief source in the United States. It is mined in South Dakota and in North Carolina near Kings Mountain. In both localities, it occurs associated with other minerals and is recovered by flotation. According to Bowles,[2] mill capacity for spodumene concentrate was 2000 tons a month at the end of 1943. Another important source is Searles Lake brine from which lithium sodium phosphate is recovered. About 300 tons of this material was shipped in 1938. Some lepidolite is also produced in the United States, but most of this goes directly into glass and ceramic manufacture, very little being used for the production of lithium salts.

[1] *Z. Elektrochem.*, Vol. 19, p. 444, 1913.
[2] *Mining Met.*, Vol. 25, p. 85, 1944.

Lithium is extracted from silicate minerals by heating a mixture of the finely powdered material with an excess of potassium sulphate to a moderate red heat, care being taken to keep the temperature below the melting point of any of the constituents of the mixture.[1] An exchange reaction takes place, the potassium replacing the lithium which is converted to a soluble sulphate. The cooled mass is leached with water and the lithium precipitated from the solution as the carbonate, from which other salts can be made.

F. Fraas and O. C. Ralston, at the U. S. Bureau of Mines, recently worked out a process[2] in which spodumene is mixed with calcium chloride and lime and heated in a rotary kiln. The lithium is volatilized as chloride and is collected in scrubbers and Cottrell precipitators. No information is available as to whether this process has yet been applied commercially.

Metallurgy. 1. *Thermal.*—Unlike the other alkali metals, lithium oxide or carbonate cannot be reduced to metal by carbon since a stable carbide is formed. Mellor[3] states that metallic calcium will reduce the chloride but that the resulting alloy contains 3 to 4 per cent calcium which is difficult to separate. He also states that the hydroxide cannot be reduced by magnesium because the reaction proceeds with explosive violence. This is to be doubted. Hackspill and Pinck[4] found that magnesium, aluminum, and iron reduce lithium oxide in high vacuum. The reaction with magnesium takes place at 450°, with aluminum at 1150°, while that with iron is incomplete at 1300°.

Thermal processes have so far not been important in the metallurgy of lithium. Unlike sodium and potassium, commercial production developed after the introduction of the electric generator.

2. *Electrolytic.*—Like sodium and potassium, lithium has not been deposited directly from aqueous solutions. However, as in the case of the other two, amalgams can be prepared.

At the present time, the metal is produced commercially by the electrolysis of its fused chloride. According to Osborg (*op. cit.*), the pure chloride is unsuitable even though it has a comparatively low melting point, 610°. The voltage soon rises and electrolysis ceases. However, the addition of KCl overcomes these difficulties, and this bath operates continuously in large units and at high yields. Current efficiency is high, over 90 per cent, and the lithium recovery, based on LiCl fed, is over 95 per cent.

To ensure pure metal, the chloride must be pure, the cells constructed of materials that are not attacked by the highly corrosive bath, and the metal itself protected from the nitrogen of the air with which it readily combines. As a result of controlling these factors, the purity of the metal has reached 99.5 per cent with a nitrogen content of 0.03 per cent. The lithium chloride should be free from water before it is added to the cell. Izgaruishev and Pletnev[5] as a result of work with a 225-amp. cell recommend a 1:1 mixture of LiCl and KCl as electrolyte with iron cathodes and graphite anodes. They give the cell voltage as 17, current efficiency as 85 per cent, and the direct-current power consumption as 34 kw.-hr. per lb. (75 kw.-hr. per kg.). The voltage appears to be much too high.

An interesting method of preparing lithium is due to L. Kahlenberg.[6] He electrolyzed a concentrated solution of LiCl in pyridine. Using a carbon anode and a bright iron cathode, and a current density of 0.2 to 0.3 amp. per sq. cm. (1.9 to 2.8 amp. per sq. ft.), he secured a dense, silver white. adherent deposit of metallic lithium.

[1] Osborg, monograph "Lithium," Electrochemical Society, 1935.

[2] *Bur. Mines Rept. Investigations* 3344.

[3] "Comprehensive Treatise on Inorganic and Physical Chemistry," Vol. 2, p. 450.

[4] *Bull. soc. chim. France*, Vol. 49, pp. 54–70, 1931.

[5] *Izvestiia Metal*, p. 536, 1932.

[6] *Jour. Phys. Chem.*, Vol. 3, p. 601, 1899.

The potential drop across the cell was 14 volts. Lithium chloride is very soluble in a number of organic solvents.

Production, Prices, and Uses.—No published information as to production has been found since 1929, when it was stated[1] that the United States production was 100 lb. per day. It has probably increased since that time. According to recent quotations, the price for 98 to 99 per cent metal is $15 per lb. in 100-lb. lots.

Osborg (*op. cit.*) lists a large number of possible uses for lithium. Among these are the preparation of oxygen-free copper of high electrical conductivity and the degassing and purification of copper and copper-base alloy castings. Master alloys are commercially available for greater convenience in adding the lithium. Other suggested uses are the treatment of iron and stainless steel and as an alloying uent with aluminum, lead, magnesium, and zinc. Some years ago, a lead-b ing alloy was developed in Germany and found extensive use. Called "B-Me contained approximately 0.04 per cent Li, 0.66 Na, 0.73 Ca, 0.03 K, less than cent Al, balance lead. An aluminum-base alloy, Scleron, which contained lit was also placed on the market in Germany for structural uses. Its composition was 83 Al, 12 Zn, 2 Cu, 0.5 to 1 Mn, 0.5 Fe, 0.5 Si, 0.1 Li.

An interesting compound of lithium, prepared by heating the metal in hydrogen, is the hydride, LiH, to which reference was made in the introduction to this section. It is a solid with a melting point of 680° and reacts with water to liberate hydrogen. It has been proposed as a means of transporting this gas, as 1 lb., reacting with water, yields about 45 cu. ft., at ordinary temperature and pressure. It also reacts readily with other substances.

The metal also has possible applications in organic chemistry.

A recently announced metallurgical use for lithium compounds is their addition to the atmospheres of steel heat-treating furnaces. It is claimed that their presence prevents scaling and decarburization of the steel during treatment.

CESIUM

Cesium is the most electropositive and the most reactive at ordinary temperatures of all the metals.

Occurrence.—Cesium is the rarest of all the elements considered in this chapter. It is present in the earth's crust to the extent of about 0.000008 per cent, approximately the same as cadmium, mercury, and iodine. It is widely distributed and occurs in some mineral springs and in minute amounts in sea water.

The principal mineral source is pollucite, $H_2Cs_4Al_4(SiO_3)_9$, the only cesium mineral known. It occurs on the island of Elba, where it was first discovered.

For a time the only commercial deposit in the United States was in Maine, but in 1938, an important strike at the Tin Mountain mine in South Dakota was announced.[2] By the end of that year, over 100,000 lb. of ore containing 1 to 30 per cent Cs_2O had been produced.

Cesium can be extracted from the finely ground mineral by digestion with strong hydrochloric acid. The resultant solution is treated with a solution of antimony trichloride to precipitate the cesium as a complex chloride.

Lepidolite frequently contains significant amounts of cesium which can be recovered as a by-product when the mineral is treated for lithium.

Metallurgy. 1. *Thermal.*—Cesium metal can be produced by reduction of the carbonate with carbon, but like potassium, it forms an explosive compound with carbon monoxide. It can also be prepared by reduction of the chloride with calcium or calcium carbide or of the hydroxide with aluminum or magnesium. In all these pro-

[1] *Mining Met.*, Vol. 11, p. 47, 1930.
[2] *Mining Met.*, Vol. 20, p. 9, 1939.

cesses the metal is liberated as vapor and condensed. Reduction of the chloride by calcium, which has been described by Hackspill,[1] appears to be the simplest process as no gas is evolved and the entire operation can be conducted in a vacuum. Polyakov and Fedorov[2] tried calcium carbide instead of the metal and obtained 75 per cent recovery of the cesium as metal. However, the reduction of the hydroxide by magnesium, investigated and fully described by Erdmann and Menke[3] and by Richards and Brink,[4] appears to be equally efficient provided certain precautions are observed. The reaction is carried out at a red heat in an iron tube through which a current of dry hydrogen is passed, and care must be taken to avoid too rapid heating and to maintain a flow of hydrogen.

Hackspill and Pinck[5] found that the sulphate, arsenate, thiocyanate, and other salts could be reduced by iron in a vacuum. The sulphate and arsenate were reduced at their melting points, the thiocyanate at 650°, while the borate and phosphate required temperatures of 1300 to 1400°C.

2. *Electrolytic.*—As in the case of potassium, cesium amalgam can be prepared from aqueous salt solutions, but the metal itself has not been deposited. It has been prepared by electrolysis of a fused mixture of cesium and barium cyanides.

Production, Prices, and Uses.—There is no available information as to production and prices. However, the total United States production of the metal and its salts probably does not exceed 500 lb. per year. Small though this is, it is very important because of the uses of the metal in electronics. Cesium is the only metal that gives off electrons when it is exposed to visible light of all colors. It is therefore widely used in photoelectric cells. Furthermore, by depositing exceedingly thin layers of cesium and oxygen on silver, a surface is obtained that is not only much more sensitive than one of pure cesium, but its sensitivity extends far into the infrared region of the spectrum. Because of these properties, this surface is used in the modern television camera and in "black light" signaling devices.

Another valuable property of the cesium-oxygen-silver surface is its efficiency as a secondary electron emitter. When struck by an electron, it gives off as many as nine secondary electrons, and it is therefore used in an extraordinary amplifying device called the "electron multiplier." Amplifications of as high as 5 million have been obtained in 10 stages with this instrument.

RUBIDIUM

Rubidium is the least important, economically, of the alkali metals.

Occurrence.—Rubidium is about ten times as abundant as cesium, but up to the present, no mineral of which it is a major constituent has been found. It has been found in sea water, mineral springs, carnallite from the Stassfurt deposits, and in lepidolite. The last is the principal source, but reasonable quantities could be recovered from the Stassfurt mother liquors if a demand were to develop.

Metallurgy.—The methods described for the preparation of metallic cesium apply equally to rubidium with only one possible exception, the electrolysis of the fused cyanide. However, rubidium has been prepared by the electrolysis of its fused hydroxide.

Production, Prices, and Uses.—There is no published information about production or prices. The metal has no use of any importance. It suffers from the fact that most of its properties are intermediate between those of potassium and cesium.

[1] *Compt. rend.*, Vol. 141, p. 106, 1905.
[2] *Jour. Applied Chem.* (*U.S.S.R.*), Vol. 13, p. 1833, 1940.
[3] *Jour. Am. Chem. Soc.*, Vol. 21, p. 259, 1899.
[4] *Ibid.*, Vol. 29, p. 125, 1907.
[5] *Bull. soc. chim.*, Vol. 49, p. 54, 1931.

THE ALKALINE-EARTH METALS

The alkaline-earth metals, in the order of their economic importance, are calcium, barium, and strontium. Radium also belongs to this group, but it will not be discussed in this chapter as it is important for its radioactive properties and is used only in the form of its salts. (See Chap. XXIII.)

These metals are silvery white, malleable, and comparatively soft, although calcium, probably the hardest, is considerably harder than lead. Although second only to the alkali metals in electropositive character, they differ markedly from them. They have much better physical properties, higher melting and boiling points, and are generally less reactive at ordinary temperatures. Calcium, for instance, is moderately stable in the air, decomposes water only slowly, and is not attacked by alcohol. However, reactivity increases with atomic weight, and barium is about as active as lithium.

Strangely enough these metals are not so easy to produce as those of the alkali group. There are a number of reasons for this, among which are their high melting and boiling points, their great reactivities at high temperatures, and the fact that they form stable carbides, nitrides, and silicides. It is even more difficult to purify them as, in the liquid state, they dissolve not only other metals but also their own nitrides and silicides. Indeed it is only in recent years that even calcium has been prepared reasonably free from nitrogen. As a result only the latest determinations of physical properties are likely to be reliable. The situation is even worse in the cases of strontium and barium.

The salts of these metals, like those of the alkalies, are generally colorless except where the acid radical is colored. On the other hand, many more of them are insoluble or only sparingly soluble. Among the most important compounds in this class are the hydroxides, carbonates, fluorides, sulphates, and silicates. Because of the less

TABLE 2.—PHYSICAL PROPERTIES OF ALKALINE-EARTH METALS

	Ca	Sr	Ba
Atomic weight	40.08	87.63	137.36
Specific gravity 20°C	1.54	2.6	3.5
Coefficient of expansion per °C. at room temperature, $\times 10^{-6}$	25		
Melting point, °C	851	771	704
Boiling point, °C	1487	1384	1638
Heat of fusion, cal. per g	55.7	25.0	10.2
Heat of vaporization, cal. per g	911	383	260
Specific heat, room temp., cal. pe g	0.157		0.68
Electrical resistivity,[1] 0°C	3.43	22.76 (20°)	
Ultimate tensile strength, lb. per sq. in.[2]	6300		
Proportional limit, lb. per sq. in.	1500		
Elongation, per cent	53		
Reduction in area, per cent	62		
Hardness, Brinell	13		
Modulus of elasticity, lb. per sq. in.	2,900,000–3,700,000		

[1] Microhms per centimeter-cube.

[2] Mechanical properties are from *Nat. Bur. Standards Circ.* C 447 and were determined on distilled metal containing 99.3 per cent Ca, 0.14 per cent Si, 0.02 per cent Fe.

electropositive character of these metals, their salts with weak acids are more readily decomposed and those with strong acids show some tendency to hydrolyze in the presence of water. The hydroxide and carbonate of calcium, for instance, are readily converted to the oxide by heating, and it is difficult to prepare anhydrous calcium chloride because of hydrolysis. However, the metals become more electropositive with increasing atomic weight, and barium salts are much more stable. To convert barium carbonate to the oxide, it must be heated with coke to reduce the carbon dioxide, and barium chloride can be readily dehydrated.

These metals form saltlike hydrides and dissolve in liquid ammonia like the alkali metals. Their salts impart characteristic colors to the Bunsen flame.

Physical Properties.—All these metals crystallize in the cubic system at ordinary temperatures, calcium and strontium with face-centered lattices and barium with a body-centered lattice. Calcium and barium show polymorphism. The transition point for calcium is at 450°C., with a possible second one at 300°, while that for barium is at 375°. The high-temperature form of calcium is hexagonal, close packed. So far, no evidence of a transition has been found for strontium. The physical properties of the metals are summarized in Table 2.

CALCIUM

This metal is the most important of its group.

Occurrence.—Calcium is the fifth most abundant element, constituting, according to F. W. Clarke, 3.64 per cent of the earth's crust. The most important source of the metal and its compounds is, of course, calcium carbonate in its various forms, limestone, marble, oyster shells. Large deposits of these materials are found in all parts of the globe. Other calcium minerals occur in economic quantities, but except for calcium fluoride, the mineral fluorite or fluorspar, which is sometimes added to the electrolytic bath, none are important in its metallurgy.

Calcium carbonate, when heated to a high temperature, gives off carbon dioxide and is converted to calcium oxide, quicklime, or simply lime, the most important industrial alkali. Thousands of tons of lime are made daily in rotary kilns and shaft furnaces.

Some 2 to 3 million tons of calcium chloride a year are potentially available in the residual liquors from the ammonia-soda or Solvay process. Some is recovered for a number of uses, but the greater part is run to waste.

The raw materials for calcium production are therefore abundant.

Metallurgy. 1. *Thermal.*—Calcium can be prepared by a number of thermal methods. Moissan made it by heating the anhydrous iodide with sodium to produce a sodium-calcium alloy. Treatment with alcohol dissolved the sodium, leaving calcium of about 99.3 per cent purity.

According to a number of recent patents,[1] calcium can be produced by heating calcium oxide with silicon or aluminum in an evacuated retort in a manner similar to the production of magnesium. As in the other process, the addition of a small amount of a fluoride, 0.5 to 5 per cent, is said to promote the reaction. That calcium can be produced in this way is not surprising, as Gunz and Matignon used it to produce metallic barium over thirty years ago.

A recent United States patent[2] claims that the reduction with silicon can be carried out in an arc furnace.

The fact that lime can be reduced with silicon probably means that it can also be reduced by calcium silicide, an electric-furnace product, with resulting increased yield,

[1] British patent 497772, Dec. 28, 1938, to Magnesium Elektron, Ltd.; French patent 830187 to I. G. Farben.

[2] U. S. patent 2225536.

and that the silicide itself will dissociate on heating *in vacuo* to produce calcium and silicon.

As a result of the experience gained with magnesium, these processes may become very important as sources of calcium in the not far distant future. One advantage of calcium over magnesium lies in its higher equivalent weight: 20 lb. of calcium require only as much reducing agent as 12 lb. of magnesium at the same efficiency.

The metal can also be produced by reduction of lime with carbon. This is far more difficult and complicated than in the case of the alkali metals and, so far as is known, has not been worked on a commercial or even on a large pilot-plant basis. The method is a two-stage one. When lime and coke are smelted in an electric furnace, the product is calcium carbide. This is produced on a large scale as a source of acetylene and other products. It has been known for some time that, when heated to a very high temperature, calcium carbide dissociates into graphite and calcium vapor. The vapor pressure of the calcium has been measured. Recently, Manderli, Moser, and Treadwell[1] produced compact calcium by heating the carbide to 1600 to 1800°C. in a vacuum.

Hanawalt, Nelson, and Ward[2] have patented processes in which calcium carbide is heated with calcium silicide or with metallic iron. The calcium distills off, leaving a residue of silicon carbide or of carburized iron.

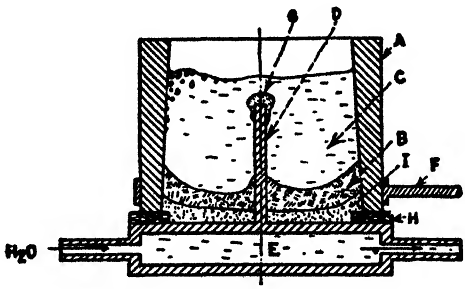


FIG. 3.—Submerged cathode cell.

Calcium carbide is now being used to make calcium-lead alloys. By heating it with lead under a chloride flux, alloys containing 3 to 4 per cent calcium are obtained.

2. *Electrolytic.*—Calcium, like the alkali metals, has not been deposited from aqueous solutions, but, also like them, amalgams can be produced by using a mercury cathode. A crude metal, probably a high-calcium amalgam, has been obtained in this way on a small scale.

Most of the commercial calcium on the market at the present time is produced by the electrolysis of its fused chloride. This is not an easy operation. It is difficult to prepare the anhydrous chloride free from basic salts and oxide, and apparently, it has not yet been found possible to run a calcium cell on hydrated feed as is done with magnesium. Another difficulty is the high melting point of calcium (851°C.). Although this is reduced to the neighborhood of 800°C. by impurities, the bath would have to be operated at about 900° if liquid metal were to be tapped off, a temperature at which the metal reacts vigorously with air to form oxide and nitride which rapidly thicken the bath and render it useless. Furthermore, at this temperature, the metal rapidly diffuses through the bath, becomes chlorinated at the anode as rapidly as it is deposited at the cathode, and electrolysis soon stops. Attempts to operate below the melting point of the metal yield only a voluminous sponge, which grows rapidly to the anode and is so full of electrolyte that it is of little or no value.

[1] *Helvetica Chim. Acta*, Vol. 27, p. 105, 1944.

[2] U. S. patents 2122419, 2122420, 2122446.

The electrodeposition problem was solved by Rathenau with his contact cathode. This is a round steel bar or pipe which is placed vertically in the cell and can be moved up or down. It may be water cooled. In operation it is set so that its lower end just touches the surface of the bath. The resultant high current density raises the temperature in the neighborhood of the cathode above the melting point of calcium, causing the metal to be deposited in the molten state. If conditions are correct, the calcium wets the steel and will adhere to it when it is raised. This is done slowly, and the metal solidifies a short distance above the bath level. Continuation of the upward movement causes more metal to be drawn up and to solidify so that a vertical rod of calcium is slowly built up. The lower end of the calcium, therefore, quickly becomes the real cathode, the steel serving merely as a lead for the current. The metal, as it leaves the bath, becomes coated with a thin layer of molten electrolyte which soon solidifies and serves as a protective coating. As electrolysis proceeds, the

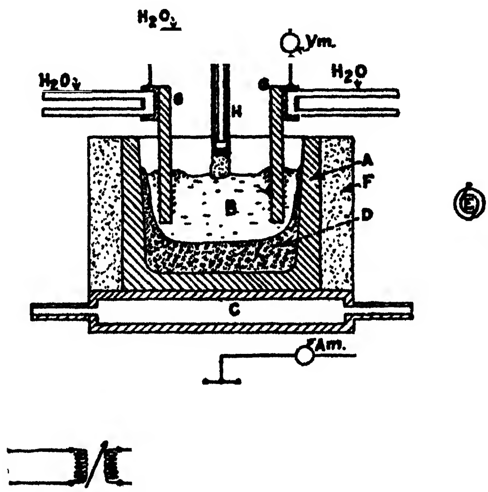


Fig. 4.—Improved Rathenau cell.

lower end of the calcium becomes larger until an equilibrium size is reached, with the result that the deposited metal acquires a roughly conical shape. Because of this shape, the lump of crude metal is known as a "carrot."

The speed with which the cathode is raised is critical. If it is much too great, contact is broken immediately. If not quite so great, the deposit becomes smaller in diameter, the current density and temperature rise, the metal stays molten farther above the bath level, convection currents become more violent, and eventually contact is broken. If too slow, the temperature drops below the melting point of the metal and a spongy deposit is obtained. In the early days of calcium production, regulation of the cathode was manual, but recently automatic controls have been developed.

When the cathode has reached the end of its travel upward, electrolysis is stopped, the carrot is removed, the steel cathode lowered, and the process repeated. The carrots produced from the latest cells range in size from 7 to 14 in. in diameter and 7 to 25 in. in length.[1]

The anode material is graphite. Some experimenters have recommended that the cell lining be made of this material and used as the anode, but Brace[2] used separate anodes which could be moved about to control the voltage drop and therefore the

[1] Kinzel, *Mining Met.*, Vol. 22, p. 488, 1941.

[2] *Trans. Electrochem. Soc.*, Vol. 37, p. 465; 1920.

temperature of the bath to some extent independently of that at the cathode. The largest United States producer adopted this idea in a pilot-plant cell, but it is not known whether it is being used on a large scale.

The electrolyte used in commercial European practice is a mixture of calcium chloride and fluoride. Some workers have recommended potassium chloride, instead of calcium fluoride, while Frary, Bicknell, and Tronson,[1] and Brace prefer the pure chloride on the basis that the melting point of the bath should not be too far below that of the metal. According to Mantell and Hardy,[2] the operating temperature of the bath is between 780 and 800°C. They also state that the bath must be skimmed at intervals and occasionally discarded owing to accumulation of impurities.

Cells with capacities up to 10,000 amp. are now in operation in the United States. They are probably more efficient than the smaller European cells which ha

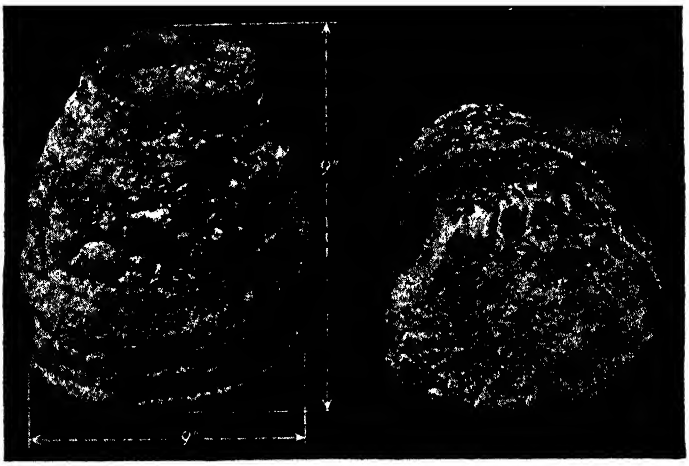


FIG. 5.—A calcium carrot. (*Courtesy of Dr. A. B. Kinsel.*)

energy consumption of about 23 kw.-hr. per lb. of metal produced. However, a higher energy consumption is inherent in this process owing to the large potential drop at the contact cathode.

The present calcium cell has a number of disadvantages in addition to the high energy consumption. The large production of heat in the cell seriously limits its size, as this heat must be radiated. Because of the contact cathode, the top of the cell cannot be closed in and the chlorine must be swept out with a current of air. The dilution of the chlorine makes it unavailable for liquefaction, an important item since about 1.75 lb. are produced per pound of metal, and in addition presents a serious disposal problem. Furthermore, the current of air not only carries off considerable quantities of electrolyte as spray, but its water vapor and oxygen are probably chiefly responsible for the deterioration of the bath.

The carrots produced in the United States[3] contain only about 85 per cent metal, most of the remainder being electrolyte. To remove this they are melted and cast into various shapes in an atmosphere of argon. The product contains 95 to 97 per cent calcium. A higher grade of metal is produced by distillation in a retort at high vacuum. Sodium in the crude metal caused trouble in this operation by distilling over with the calcium and igniting when the retort was opened, but this difficulty was soon overcome through experience.

[1] *Trans. Electrochem. Soc.*, Vol. 18, p. 117, 1910.
[2] *Metals & Alloys*, Vol. 10, p. 55, 1939.
[3] BAGLEY, *Chem. Eng. News*, Vol. 22, p. 921, 1944.

Production and Prices.—Prior to 1939, practically all the calcium used in the United States was imported from France. The amount of these imports, taken from the "Minerals Yearbook," are shown in Table 3. Production in the United States began in the summer of 1939, has grown rapidly, and is now probably more than

TABLE 3.—IMPORTS OF CALCIUM

Year	Weight, Pounds
1937	23,767
1938	41,299
1939	41,718
1940	11,900

500,000 lb. per year. Prices have remained steady for the last few years at $1.25 a pound for 97 to 98 per cent metal in ton lots. Available forms are slabs of various sizes and cylinders, either with or without a central steel pipe, and turnings.

Uses.—Calcium has a number of important uses. It is added to magnesium alloys to the extent of about 0.25 per cent to refine grain, reduce tendency to take fire, and to simplify heat-treatment. Its property of reducing the tendency to take fire is so pronounced that specifications placed very low limits on the amount permissible in incendiary-bomb alloy. Its effect on heat-treatment is observed in those alloys containing zinc. In its absence, a two-stage treatment is necessary, one at a temperature below the melting point of the zinc-bearing constituent to dissolve this, and another at a higher temperature to dissolve the aluminum In its presence, only the high-temperature treatment is necessary.

Calcium is added to lead to harden and strengthen it. Its solid solubility in lead is 0.10 per cent at the melting point and decreases rapidly with the temperature with the result that precipitation hardening takes place. The alloy, which contains less than 0.25 per cent calcium, is used for cable sheaths and has been recommended for storage-battery grids and other purposes. Master alloys containing up to 5 per cent calcium, the balance lead, are on the market and are made by electrolysis of fused calcium chloride with a molten lead cathode, or from lead and calcium carbide.

Calcium and magnesium are used in the Betterton process for removing bismuth from lead. They form compounds with bismuth, which are insoluble in lead just above its melting point and form a dross which is skimmed off.

The metal is an excellent scavenger. It reacts readily with oxygen, nitrogen, sulphur, carbon, and many of their compounds. It has therefore been recommended as an addition to both ferrous and nonferrous alloys. Its affinity for oxygen makes it a powerful reducing agent, and Marden and Rich have worked out a process in which it is used to reduce the oxides of vanadium, uranium, thorium, and other refractory metals. Calcium chloride is added as a flux. The metals produced are malleable and ductile and fully equal in properties to those made by the action of sodium on the anhydrous chlorides which are difficult to prepare and to handle.

Calcium hydride is being made commercially by the action of hydrogen on the metal and is being used for the reduction of refractory oxides, such as those of titanium, zirconium, and uranium, to produce commercial grades of these metals and their alloys with the more common metals.

BARIUM

Barium is the eighteenth most abundant element, being present in the earth's crust to the extent of about 0.04 per cent. Its principal minerals are the sulphate, barite, and the carbonate, witherite. Witherite is preferred as it is readily soluble in acids to form other barium salts, but barite is more available. To produce other barium salts from barite, it is heated in a rotary kiln with carbon to reduce it to the

sulphide which is dissolved in water and treated with carbon dioxide gas or with soda ash to precipitate the carbonate. As already mentioned, barium carbonate is not readily converted to oxide. To accomplish this, it is mixed with carbon and heated, with the result that the carbon dioxide is reduced to monoxide and goes off.

Barium chloride is readily prepared by dissolving the carbonate in hydrochloric acid. It can be readily prepared in the anhydrous state as it is not nearly so soluble as calcium chloride and crystallizes with only two molecules of water which can be driven off at a low temperature without hydrolysis.

Metallurgy. 1. *Thermal.*—Barium can be produced by reduction of the oxide with aluminum in an evacuated retort. Guntz[1] used this method in 1906. A reference to a Russian article[2] gives some details of the process. A vertical retort is equipped with a water-cooled condenser and heated by an electric furnace. The apparatus is 23 cm. in diameter at the bottom and 50 cm. high. The temperature of distillation is 1050°C. and the yield per batch, 304 g. of metal containing 99.41 per cent barium and a total of 0.071 per cent copper manganese and aluminum. The condensed barium is removed in a carbon dioxide stream and sealed in iron cylinders. The same apparatus can be used for production of barium, magnesium, strontium, and calcium and their alloys.

The barium is usually recovered as a solid in this process, but a recent patent,[3] specifies keeping the condenser at a temperature between 730 and 800°C., whereby the metal is condensed to liquid and, still under vacuum, allowed to run to a receiver where it solidifies. Another French patent[4] specifies a ratio of barium oxide to aluminum of 4:2 and states that up to 2 per cent barium fluoride may be added to promote the reaction. The patents to which reference was made in discussing the reduction of calcium by aluminum also cover barium.

Danner[5] describes a variation of this process in which an oxide containing about 10 per cent barium peroxide is used. The reduction reaction is carried out in a separate vessel, the heat required being supplied by the reaction of the peroxide with part of the aluminum. The barium is recovered from the resulting sintered mass by distillation *in vacuo*.

Matignon[6] found that barium oxide could also be reduced by silicon. He used a mixture containing three parts of the oxide to one of silicon, formed the mixture into briquettes, and heated at 1200°C. in an evacuated steel tube. The metal obtained was 98.5 per cent pure, and the residue in the retort contained barium silicate. In another experiment, he used 90 per cent ferrosilicon with equally good results.

All the patents referred to above also cover the use of silicon as a reducing agent. The ratio of barium oxide to silicon is given as 4:1.[4]

2. *Electrolytic.*—As in the case of calcium, barium has not yet been deposited from aqueous solutions. However, an amalgam can be made, and Guntz[7] first prepared a comparatively pure barium metal in this way. He heated the amalgam to drive off most of the mercury, heated the residue in hydrogen to convert the barium to the hydride and drive off the rest of the mercury, and finally decomposed the hydride *in vacuo* at a high temperature, the barium metal condensing on a water-cooled surface.

Neumann and Bergve[8] state that they produced metallic barium from fused barium chloride, using a contact cathode similar to that used for calcium, but give

[1] *Compt. rend.*, Vol. 143, p. 339, 1906.
[2] *Chem. Abstracts*, Vol. 34, p. 7181, 1940.
[3] French patent, 831083 to I. G. Farben.
[4] French patent, 831598 to I. G. Farben.
[5] *Jour. Am. Chem. Soc.*, Vol. 46, p. 2382, 1924.
[6] *Compt. rend.*, Vol. 156, p. 1378, 1913.
[7] *Compt. rend.*, Vol. 141, p. 1240, 1905.
[8] *Z. Elektrochem.*, Vol. 20, p. 187, 1914.

no details on the procedure. It is probable that all the barium on the market is being produced by aluminum or silicon reduction.

Production and Prices.—No information is available as to the production of barium or current prices.

Uses.—Barium, either alone or as an alloy with magnesium or aluminum, is widely used as a "getter" to remove residual gases from electron tubes. It is stated to be ten times as efficient as magnesium for this work. A barium-nickel alloy is being used for the terminals of spark plugs.[1] The alloy contains up to 0.2 per cent barium and reduces the potential required to produce a spark across the gap. An alloy containing about 1 per cent barium has been found to be an efficient emitter of electrons when heated and for this reason has been suggested for use in vacuum tubes. Nickel alloys containing up to 1½ per cent barium are ductile and may be easily rolled or drawn into fine wire or ribbon. A recent use for barium is as a lubricant for rotating anodes in X-ray tubes. Ordinary lubricants cannot be used as the temperature is high, about 600°C., and their vapors cannot be tolerated in the tube. Barium has a low vapor pressure at that temperature and shows excellent lubricating qualities.

STRONTIUM

Strontium is about 40 per cent as abundant as barium, and like that metal, its chief minerals are the carbonate, strontianite, and the sulphate, celestite. Again the sulphate is more abundant and serves as the major source of strontium salts.

Before 1940, practically all the celestite used in the United States was imported from England as the domestic deposits were either remote from transportation or of low grade. However, since that time domestic sources have been developed and are supplying the increased demand due to the war.

Strontium salts are manufactured from the minerals by the same methods used for barium salts. Strontium carbonate is more readily converted to the oxide than barium carbonate, and the operation is conducted in the same manner as with limestone.

Metallurgy. 1. *Thermal.*—The methods used for barium can be used equally well for strontium. Guntz and Galliot[2] reduced the oxide by mixing the finely ground material with powdered aluminum and heating in an evacuated iron tube for 4 hr. at 1000°C. Metal of 99.4 per cent purity was recovered as a crust, with a yield of 75 per cent. The method in which strontium peroxide is added to the charge and the reaction and distillation are carried out in separate containers has been used commercially.

2. *Electrolytic.*—Strontium amalgam can be made from aqueous solutions, but it has not yet been found possible to deposit the pure metal.

Neumann and Bergve[3] prepared strontium by the electrolysis of a fused mixture containing 84 per cent strontium chloride and 16 per cent potassium chloride. They used the contact electrode and secured a current efficiency of 80 per cent.

Production and Prices.—There is no available current information on these subjects. Some fourteen years ago, a figure of $100 a pound was published. Four years later it was stated that the price was still over $30.

Uses.—Strontium occupies the same position among the alkaline-earth metals as rubidium does among the alkalies, *i.e.*, it is intermediate in its properties between barium and calcium. About fifteen years ago, metallic strontium was in comparatively large demand as a "getter" for radio tubes, but it has since been supplanted by barium and its importance as well as its production has fallen off.

[1] *Trans. Electrochem. Soc.*, Vol. 66, p. 85, 1934.

[2] *Compt. rend.*, Vol. 151, p. 813, 1910.

[3] *Z. Electrochem.*, Vol. 20, p. 187, 1914.

CHAPTER IV

ARSENIC

By Walter C. Smith[1]

Arsenic was not recognized as a metallic element until it was isolated by Schroeder in 1694; several of its compounds, however, were known from antiquity and were called arsenic. The name arsenic is used even today when the arsenious oxide is meant. Metallic arsenic is not used in the arts to a great extent, while the arsenious oxide (white arsenic of commerce) has many uses.

Physical Properties.—The metal has a steel-gray color and shows a brilliant luster on fresh fracture; it is known in both the crystalline and amorphous states. The crystalline form is very brittle Other physical properties are: atomic weight, 74.96; number by Moseley's arrangement, 33; specific gravity, (crystalline) 5.727, (amorphous) 4.71; fracture, coarsely crystalline; crystallization, hexagonal; melting point, red heat under pressure in the absence of oxygen; boiling point, volatile at 450°C. without melting; specific heat, (crystalline) Sm, 0.083; (amorphous) Sm, 0.0758; latent heat of sublimation, 60 cal. per g.

Chemical Properties.—Arsenic is not changed in dry air, but in moist air it loses its color and brilliancy and slowly changes into arsenious oxide. It burns with a bluish-white flame when heated in air and gives off heavy white fumes of arsenious oxide, which have a characteristic odor resembling garlic.

Nitric acid oxidizes arsenic to arsenious oxide and then to arsenic oxide. Aqua regia yields a mixture of arsenious and arsenic compounds. Arsenic is soluble in hot concentrated sulphuric acid, but dilute acid does not attack it. Hydrochloric acid attacks it in the presence of air, feebly, to form arsenious chloride. It combines directly with chlorine to form arsenious chloride. It also combines directly with sulphur, when heated, to form arsenic sulphide. Metallic arsenic yields potassium arsenate when heated with niter or potassium chlorate.

In solution, silver will replace arsenic and vice versa, depending upon conditions, but Fe, Ni, Co, Cr, and Mo will not replace arsenic to a notable extent under any conditions. The single potential of arsenic (*vs.* calomel electrode = 0.577 volt) was found to be 0.55 in an $AsCl_3$ solution of 1 g.-equivalent of arsenic per liter and 0.54 volt in a corresponding solution of AsI_3.

Uses.—As already indicated, only limited quantities of metallic arsenic are used. A small amount of arsenic is added to lead in making lead shot, as it tends to prevent the formation of imperfect shot when the molten metal is dropped in the shot tower. A very small percentage of arsenic added to steel produces a metal that will take an extremely high polish. Arsenical copper is claimed to possess superior properties to pure copper for certain rolling and drawing operations.

The chief arsenic compound of commerce is the arsenious oxide (As_2O_3), trioxide, or white arsenic. This is used in the manufacture of glass, in the textile and paint industries, and in the manufacture of weed killers, insecticides, and medicines.

A small amount of arsenic is added to the low tin wiping solders to improve their working properties. Arsenic is added to lead, antimony, and silver alloys for use as

[1] Metallurgist, Cerro de Pasco Copper Corp., New York.

insoluble anodes in the electrolytic recovery of copper from acid sulphate solutions to increase the anode life.

Arsenical preparations furnish the most effective means of control against the cotton boll weevil, the cotton worm, the codling and the gypsy moth, and they are used for soil treatment to destroy Japanese beetle grubs. It is estimated that insecticides take 68 per cent of the arsenic used in the United States; weed killers, 19; glass manufacture 3; wood preservatives, 2; miscellaneous, including arsenical drugs, 1; exports, 7 per cent. Approximately 60,000,000 lb. of lead arsenate, 40,000,000 lb. of calcium arsenate, 2,000,000 lb. of paris green, besides important quantities of London purple and sodium arsenite, make up the first item.

Sources of Arsenic.—Arsenic, while not abundant, is one of the most widely disseminated of all the metallic elements. It has been found in a number of places in the native state, usually associated with other metals. It occurs as mispickel, or arsenopyrite, in many cobalt and cobalt-silver ores. Nearly all pyrite and sulphide ores of copper and lead contain more or less arsenic, and it is from these latter ores that the bulk of the American supply of arsenic is derived as a metallurgical by-product. The most important American producers of arsenic are listed as follows:

Company	Location	Source of Arsenic
Am. Smelting & Ref. Co.	Denver, Colo.	By-product lead smelting
Am. Smelting & Ref. Co.	Tacoma, Wash.	By-product copper smelting
Anaconda Copper Mining Co.	Anaconda, Mont.	By-product copper smelting
U. S. Smelting Co.	Midvale, Utah	By-product lead smelting
Rare Metal Products Co.	Belleville, N. J.	Arsenic sulphides

Metallic arsenic is produced by the sublimation of mispickel or leucopyrite in the absence of air, and by the reduction of arsenic trioxide with charcoal in cast-iron or steel retorts. The temperature and the pressure in the condensers have to be carefully controlled in order to yield the crystalline arsenic.

Previous to 1914 little or no metallic arsenic was made in the United States; about 50,000 lb. were imported annually, principally from Germany. After the First World War cut off the German supply, the Hoskins Process Development Co. of Chicago, Ill., began the manufacture of metallic arsenic to supply the American market. The arsenic of 99.5 per cent grade is made by the reduction of commercial arsenic trioxide with charcoal in a battery of four gas-fired furnaces as shown. Three of the furnaces take a charge of about 200 lb. each, and the fourth furnace holds 450 lb. of charge.[1]

The charge is mixed in a rotary mixer in the proportions of 1 lb. of charcoal to 4 lb. of arsenic trioxide. The capacity of the plant is 250 to 300 lb. per day, or not less than 4000 lb. of metallic arsenic per month.

The furnaces are built of steel pipe, surrounded by firebrick, enclosed in a steel jacket and supported on a pipe frame. The charging end of the retorts is sealed with a clay gasket in which is embedded a ¼-in. copper water pipe. The cooled surface condenses arsenic vapor and seals any leaks in the clay gasket. At the back of and attached to the retort is a water-cooled condenser, which is vented by means of a water seal so as to allow the escape of the uncondensed gases. Figure 2 shows the left side of one of the furnaces. Two condensers are shown in the background of Fig. 1.

[1] JONES, *Chem. & Met. Eng.*, Nov. 17, 1920.

The period of operation for the large furnace is about 10 hr., and for the smaller furnaces 7 hr. The gas is then shut off, and the retort and the condenser are allowed to cool before the condenser is opened for the removal of the metallic arsenic. Figure 3 shows the discharge end of one of the furnaces. The metallic arsenic is removed from the condenser with a bar and hammer, and is then ready for packing and shipment.

The advent of the Second World War again stopped importation of metallic arsenic from Germany. During December, 1939, the Anaconda Copper Mining Co. began production of metallic arsenic from arsenic trioxide. The plant erected for the purpose consists of six cast-iron retorts, each fitted with a condenser consisting of a condenser tee flanged to the retort and flanged to a vertical water-cooled steel-plate condenser chamber. Each retort is horizontally supported and is enclosed with firebrick. The condensers are heated by direct gas firing. The end of the retort and of the condenser tee are closed with flanged covers bolted to the retort and con-

FIG. 1.—Arsenic furnaces, with condensers in background.

denser tee with fire-clay gaskets, in which is embedded a small-diameter copper pipe for water cooling.

The retorts are charged in batches through the end with a mixture of white arsenic, the trioxide, and charcoal. The arsenic trioxide is reduced to metallic arsenic in the retort and together with some white arsenic is volatilized and is largely condensed in the form of coarse gray crystals of metallic arsenic on the retort and tee covers. A part of the volatilized metallic arsenic passes into the condenser where it deposits on the condenser walls. The condensed metal is barred down frequently and falls into the hot tee and is again volatilized. Eventually, about 80 per cent of the arsenic in the charge is recovered from the retort and tee covers in the form of coarse crystals of metallic arsenic which are packed in airtight sealed cans for shipment.

Production of White Arsenic.—The production of white arsenic is generally carried out in two stages: the production of a crude white arsenic, followed by a refining of this crude material. When arsenic-bearing materials, in which the arsenic exists in the reduced state, are roasted, the arsenic is volatilized and passes off with the gaseous products. Arsenic trioxide begins to condense at 218°C.; hence the flue products caught in the cooler parts of the flue system carry considerable arsenic. More or less

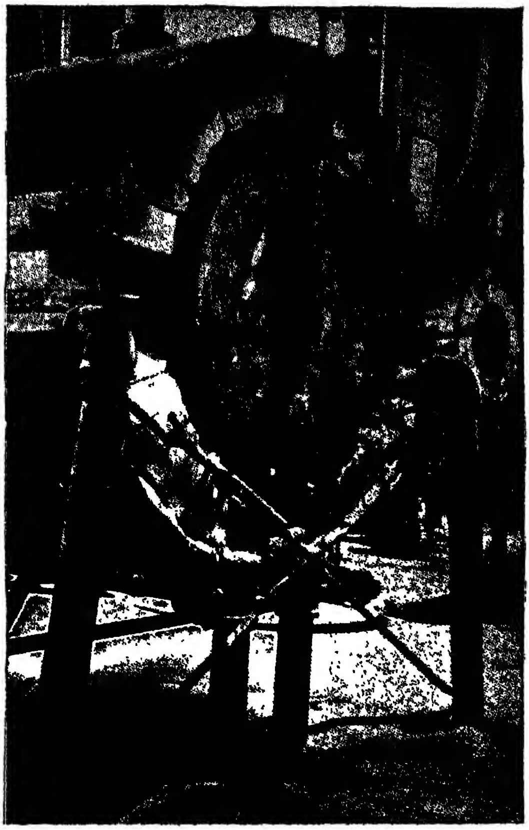


FIG. 2.—Side of arsenic furnace.

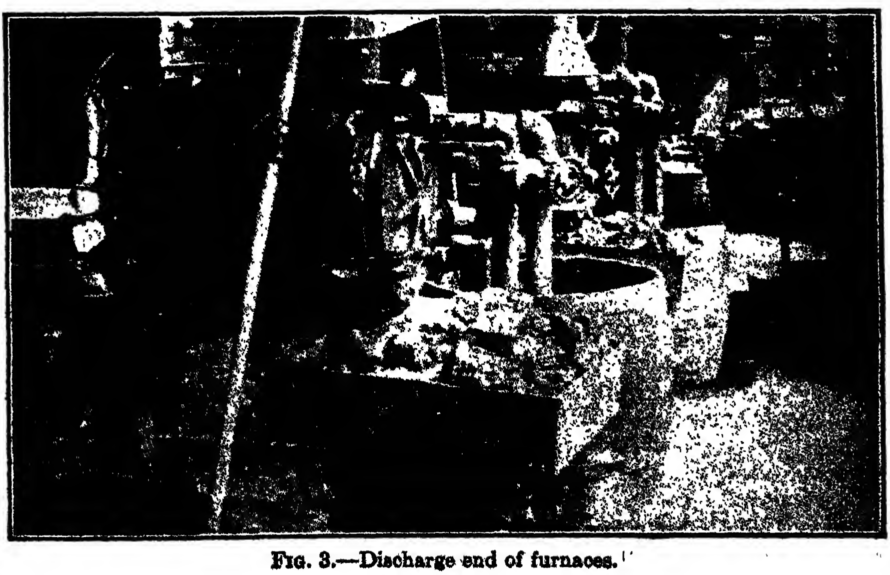


FIG. 3.—Discharge end of furnaces.

dust carried by the gases and other volatile materials can contaminate the arsenic trioxide, and these are removed in the refining operations.

The roasting operations may be carried out in muffle, reverberatory, or one of the various types of roasting furnaces; coke, gas, or oil is used for fuel in reverberatory or roasting furnaces in order to reduce the danger of contamination of the product with soot. The crude arsenic trioxide is collected in cooling flues, baghouses, or by Cottrell precipitators.

Crude White Arsenic from Metallurgical Products.—The arsenic carried by lead and copper ores is concentrated during the roasting and smelting operations in the flue products, which are caught in the cooler parts of the flue system. Lead baghouse dust, carrying 30 per cent arsenic, and copper furnace and roaster dusts, carrying 20 to 30 per cent arsenic, are not uncommon. The arsenic in these dusts exists largely in the form of the trioxide (As_2O_3).

At one of the American plants the baghouse dust, carrying about 30 per cent arsenic, is mixed with a small quantity of fine pyrite or low-grade lead sulphide concentrates and is fed to the hearth of a Brunton roasting furnace. The pyrite is added to the dust in order to prevent the formation of nonvolatile arsenites in the residue from the roast, and it also gives a clinkered residue which makes a suitable blast-furnace feed. The Brunton furnace volatilizes 75 to 90 per cent of the arsenic in the dust which is charged to it. The gases from the Brunton furnaces pass through a cooling flue built in the form of a number of connecting rooms or chambers. Brick is usually employed in the construction of these chambers, or kitchens, as they are called. The temperature of the gas in the cooling flue is so regulated that it enters the first kitchen at approximately 220°C., and by the time it reaches the last kitchen it has dropped to 100°C., or less. The crude arsenic trioxide collects in the kitchens and is removed at the end of the campaign for refining. This crude arsenic trioxide should contain 90 to 95 per cent As_2O_3.

The crude As_2O_3 is resublimed in order to remove impurities; this operation is repeated until the desired purity is obtained. Reverberatory furnaces are used for this work and are fired with gas or coke. The furnace gases pass through settling chambers and then to the kitchens, where the refined arsenic trioxide is collected. The product should contain over 99 per cent As_2O_3.

The main source of arsenic at Anaconda is in Butte copper ores. The concentrates from these ores average approximately 2.0 per cent As. The roasting and smelting operations eliminate a very considerable portion of the arsenic into the flue system where it becomes considerably concentrated in the dust collected at the Cottrell treaters and in the upper portion of the main flue. The Cottrell dust and the arsenic-enriched portion of the main flue dust constitute the feed to the arsenic roasters.

Arsenic Roasting Plant.—Three rows of McDougal roasters in No. 1 roaster building have been remodeled into three sets of arsenic-roasting furnaces and condensing chambers. A set consists of four 16-ft. six-hearth furnaces connected in series. The first, or roasting, furnace is gas-fired on the third and fifth hearths and is equipped with a specially designed apron feeder for charging the dust. The remaining three furnaces serve as condensing chambers to collect the condensed arsenic in the form of a crude As_2O_3 product. The inside hearths have been removed and a central vertical partition installed. This partition has an opening at the bottom to permit the passage of the gases. The gases enter each condenser at the top, pass down one side of the partition and up the other, leaving at the top to enter the top of the next condenser and so on to their exit through connecting flues and a dust chamber to the flue system. The bottom sets of arms have been left in each condenser and are operated periodically to remove the collected arsenic, which is sent to the refining

furnaces. The roasting furnaces are operated at a temperature of approximately 650°C., as higher temperatures cause fusion of the condensed arsenic in the condensers. Experience has proved that 50 per cent As_2O_3 is the maximum permissible in the feed to the roasters if fusion is to be prevented. Arsenical dusts of high arsenic content are diluted with fine flue dust. It has been found that improved results are obtained when coal to the amount of 10 per cent of the weight of the dust is mixed with the roaster feed.

The roasters yield a residue containing about 5 per cent As_2O_3, which is returned to the reverberatory furnaces for the further recovery of copper and the elimination of arsenic into the flue system.

The roasting furnaces have a capacity of about 50 tons of charge per 24 hr. and yield a crude arsenic trioxide assaying about 90 per cent As_2O_3.

Refining Plant.—Two refining furnaces of the reverberatory type have been installed. Each furnace has an over-all length of 36½ ft. and a width of 14 ft.; the

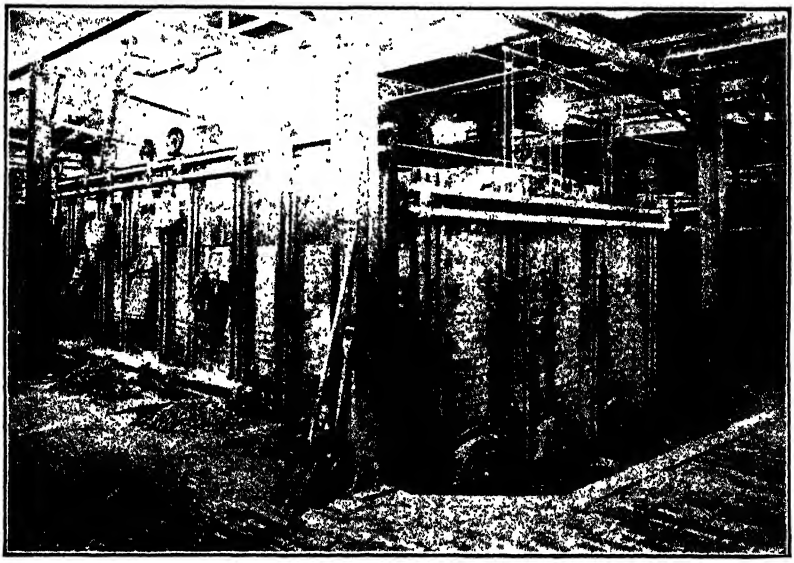


FIG. 4.—Arsenic refining furnace.

hearths are 26¾ ft. long and 12 ft. wide. The main hearths are made of cast-iron plates. Two fireboxes are used, one at the back of the furnace, whose hot gases pass under the cast-iron hearth and back over its top, and the other at the front of the furnace, whose gases pass only over the hearth.

The charge consists of 8 tons per furnace day of the 90 per cent As_2O_3 crude arsenic from the arsenic roasters. The charge is dropped to the hearth through openings in the roof and is spread out with rabbles; part of the charge is dropped during the afternoon shift and the balance during the night shift. A thin layer of crushed rock is spread over the hearth before charging the furnaces to facilitate the removal of the residue after the arsenic has been volatilized. A special crew cleans the hearths on the day shift. Each refining furnace will treat 30 tons per day, when treating very high-grade dust or when rerefining. High-grade material is dropped on all three shifts, and the residue is removed once in 2 or 3 days. A temperature of 550°C. has been found to give the best results in these furnaces. A draft of 0.05 in. of water

gives satisfactory results. The volatilization of about 80 per cent of the arsenic in the 90 per cent As_2O_3 material fed to the furnace gives the most economical operation. The refining-furnace residues are smelted in the stack reverberatory.

Condensing Kitchens.—Three sets of chambers are used for handling the gases from two refining furnaces, two of these chambers being used while the third is being cleaned. Each chamber is approximately 225 ft. long and is divided into 39 kitchens. The kitchen nearest to the furnace is larger than the others and is used for settling the nonarsenical dust. Its temperature is about 295°C., or above the condensation temperature of As_2O_3. The gases cool as they pass through the kitchens by radiation

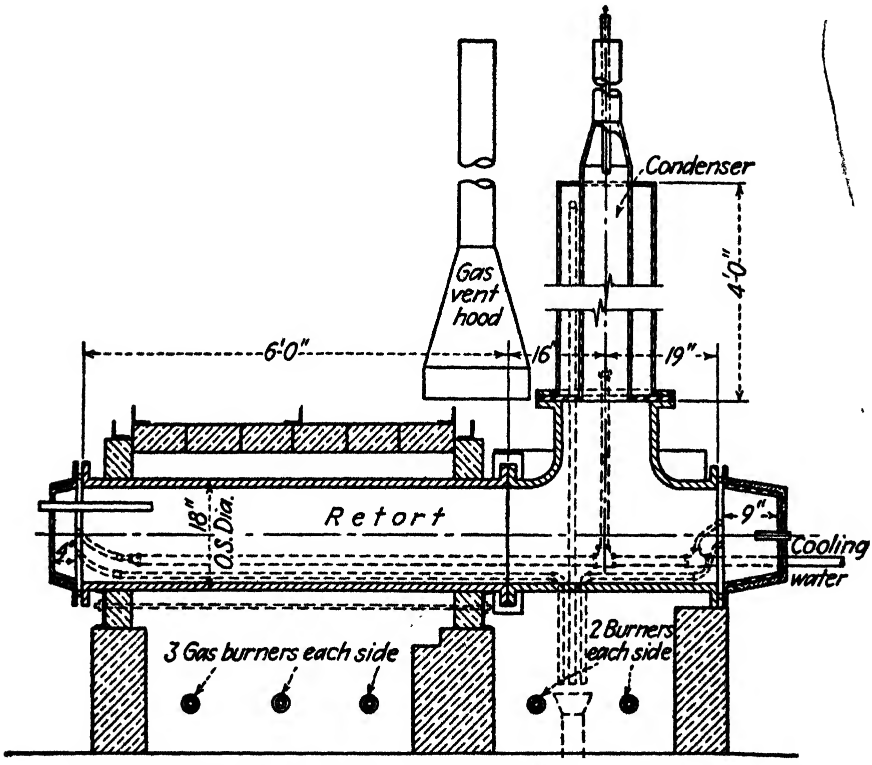


FIG. 5.—Modern refining furnace. (*Courtesy of Anaconda Copper Mining Co.*)

and leakage and leave the system at 90 to 100°C. Most of the arsenic settles out in those kitchens which have temperatures from 180 to 120°C. The kitchens nearest to the furnace contain a fused or amorphous arsenic, black in color, and carrying about 95 per cent As_2O_3. This material is rerefined. The material in the succeeding kitchens increases in arsenic content to 99.9 per cent As_2O_3, and is white and crystalline. The grade of the dust diminishes in the last kitchens, and changes to a fine white powder.

Packing.—At the end of each refining campaign the kitchens are sampled, and the samples are run for total arsenic and soluble arsenic. The product is then graded and packed in barrels of 500 lb. each; it is made into 50,000-lb. lots and sold as white soluble, white insoluble, or crude arsenic. The capacity of the packing room is 18 tons per 8-hr. day. The white insoluble arsenic can be changed to the white soluble by rerefining if market conditions demand.

Manufacture of Arsenic Trioxide from Arsenical Pyrite.[1]—The arsenical pyrite is crushed by jaw crushers and is then ground in ball mills. The ground product is washed to remove as much foreign matter as possible, and dried. The drying was formerly done on the top of the roasting furnace, but this method cools the furnace and reduces the roasting efficiency. The drying is done in a mechanical drier, which is equipped with a screw conveyer for stirring and progressing the charge.

The dried concentrate is charged to the top of a roasting furnace of the MacDougall type, 18 to 30 ft. high and 10 to 16 ft. in diameter. The rabble arms rotate at a speed of 5 r.p.m., but even at this speed some dust is carried out of the roaster with the gases, and this dust must be separated from the gases before they pass to the condensing chambers. This is done by a dust separator placed at the gas outlet of the roasting furnace. This separator consists of an insulated chamber containing two rotating screens of fine mesh provided with revolving brushes for cleaning. This arrangement removes nearly all the solid matter in the gases and offers but little resistance to the flow of the gases. The cleaned gases are then drawn by a fan through the condensing chambers.

The condensing chambers are made of sheet lead and are divided into a number of smaller compartments by sheet-lead baffles which increase the condensing surface. Water sprays are introduced into the chambers to facilitate the condensation of the arsenic trioxide and to flush the condensed material out of the chambers into a collecting tank. Lead is the only metal that will withstand the action of the sulphurous acid generated from the sulphur in the concentrate.

The mixture of water and arsenic trioxide is then filtered in vacuum filter tanks, and the moisture content is reduced to 20 to 25 per cent by the addition of some dry arsenic trioxide. It is then passed through a rotary drier, which is lined with porcelain to prevent sticking to the sides of the drier. The drying temperature employed is about 180°C., in order to prevent the loss of arsenic by sublimation during drying.

The crude arsenic trioxide is refined by sublimation. Furnaces 10 to 14 ft. in diameter, equipped with cast-iron hearths and rotating rabbles, are used for this operation. The crude arsenic trioxide is charged to the furnaces through openings in the roof. The proper temperature has been found to be 245°C. Approximately 70 parts of fuel are required for each 100 parts of refined arsenic trioxide.

The final condensation takes place in lead-lined wooden chambers containing baffles and placed over a trough that carries a porcelain screw conveyer for the removal of the collected material. About 0.65 lb. of arsenic trioxide is condensed per square foot of condensing surface. The exit gases from the condensing chambers pass to a coke-filled scrubber, where the last of the arsenic is removed with water sprays. The finished product is finely powdered, perfectly white, and will assay 99.0 per cent As_2O_3.

R. W. Bridges[2] gives the method used for the recovery of arsenic from the cobalt ores of Cobalt, Ont. The ores are crushed and then ground so as to pass 30 mesh in ball mills. The charge, with the proper fluxes, is smelted in 32 × 72 in. blast furnaces with capacities of 25 to 30 tons per day. The fluxes used are limestone and a low-grade siliceous ore. The products are flue dust and crude arsenic trioxide, slag, silver bullion, and speiss. The flue dust and crude arsenic trioxide are caught in suitable settling and condensing chambers. The flue dust is returned to the blast furnaces, and the crude arsenic trioxide is sent to the arsenic refinery for retreatment. The slag is discarded if it carries less than 10 oz. of silver per ton. The silver bullion assays about 860 fine and is treated in a cupel furnace for 24 hr., after which treatment it averages 994 fine. The speiss—a typical assay of which is Ag, 1480 oz.; As, 31.3; Co, 25.2;

[1] *Ind. chim.*, p. 426–429, December, 1920.

[2] Metallurgy of Cobalt, Ontario, Ores, *Can. Mining Jour.*, Jan. 15, 1916.

Ni, 15.3; Fe, 16.1 per cent—is crushed, ground, mixed with 20 per cent NaCl and roasted in Edwards mechanical roasters having a daily capacity per furnace of 2400 lb. The roasted product is then leached with cold water to remove the undecomposed NaCl and soluble salts of cobalt, nickel, and copper, which have formed in the roasting operation. The residue is then leached with four successive batches of $Na_2S_2O_3$ solution to remove the silver. The cobalt, nickel, and copper are recovered from the water leach liquors and the leached residues. The crude arsenic trioxide is resublimed in the arsenic refining furnaces in the usual manner, producing an arsenic trioxide of 99.0 per cent.

Manufacture of Lead Arsenate.—A number of methods have been proposed for the manufacture of lead arsenate, the first step of which is the conversion of arsenic trioxide or a soluble arsenite into arsenic acid or a soluble arsenate. A fusion of arsenic trioxide with caustic soda or sodium carbonate and sodium nitrate yields sodium arsenate, which is then dissolved in water and mixed with the solution of a soluble lead salt, as the nitrate or acetate, the insoluble lead arsenate being precipitated. Chlorine gas will slowly convert a solution of sodium arsenite into sodium arsenate; it will also convert a mixture of arsenic trioxide and water into arsenic acid. Nitric acid and arsenic trioxide react violently to form arsenic acid; the gaseous products of the reaction contain considerable nitric acid and are generally sent to a condensing system for the recovery of this acid.

A patent[1] issued to Luther and Volck covers the formation of lead arsenate by roasting the combining parts in the presence of oxygen. Lead arsenite is formed and oxidized to lead arsenate by roasting in the presence of oxygen. The lead arsenite is produced by heating white arsenic with lead or lead oxide. It may also be formed as a mixture of lead arsenite and lead arsenate by heating red lead with white arsenic. Lead arsenate may be formed directly by roasting white arsenic with lead peroxide or lead nitrate or one of the lower oxides of lead with an oxidizing agent.

The Barstow and Cavanagh patent[2] consists in combining litharge with arsenic acid assisted by the action of a catalytic agent; the direct combination of arsenic acid and litharge is too slow to be of commercial value. The catalytic agent used is a small amount of either nitric or acetic acid.

U. S. patent 1398267, issued to John Kirby, Matthew S. Hopkins, and Charles B. Bernhart, of Reading, Pa., covers the use of sulphonic acids of the aromatic hydrocarbons as catalytic agents for the manufacture of lead arsenate from litharge and arsenic acid. The purity of the sulphonic acid used is nonessential, as the mixture of sulphonic acids obtained by the sulphonation of the commercial grades of hydrocarbons will act effectively. The lead arsenate produced by the use of these reagents possesses the physical requirements important for an insecticide, *viz.*, large bulk, good dispersion, proper adherence to the foliage treated, and effective insecticidal properties.

The preparation of the catalyst is carried on approximately as follows: A commercial grade of a suitable hydrocarbon, such as ordinary naphthalene, is sulphonated in the usual manner, the excess sulphuric acid is removed by precipitation with a soluble lead salt, and the clear liquor is separated by decantation or filtration.

A charge of 700 lb. of litharge is placed in a tank and agitated to keep the litharge in suspension in water. About 50 lb. of the mixed sulphonic acids is added, the quantity to be used depending upon the speed of reaction required and the physical properties desired in the product. Approximately 600 lb. of a 75 per cent arsenic acid is then slowly added. The temperature is raised to 160°F. The mass slowly changes in color to white as the litharge is converted to lead arsenate. Any excess of litharge is removed by the addition of more arsenic acid. The resulting mass of lead arsenate,

[1] U. S. patent 929962, Aug. 3, 1909.
[2] U. S. patent 1228516, May 5, 1917.

the lead salt of the sulphonic acid, and water may be washed and the lead arsenate pressed for use as paste or as powder after drying and grinding. The sulphonic acid liberated by the precipitation of the lead arsenate is available for further use as a catalyst.

Lead carbonate or basic lead carbonate can be substituted for litharge and a solution of a soluble arsenate for the arsenic acid.

Manufacture of Calcium Arsenate.—Calcium arsenate is manufactured by the method developed by the U. S. Department of Agriculture at Tallulah, La. This consists in the oxidation of arsenic trioxide to arsenic acid by means of nitric acid. The arsenic acid is then neutralized with sodium hydrate to form sodium arsenate, and calcium arsenate is precipitated by the addition of milk of lime to the solution of sodium arsenate. The calcium arsenate produced must have the necessary physical properties for use as an insecticide.

Calcium arsenate is also made by direct combination of arsenic acid and milk of lime under controlled conditions to yield a product of the required chemical and physical properties.

Precautions in Handling Arsenic Trioxide.—Arsenic trioxide is very poisonous, and considerable care must be exercised to prevent occupational poisoning. Ample draft in the furnaces and flue systems, proper ventilation in all parts of the arsenic plant, proper bathing facilities for the men, and the use of efficient respirators have greatly reduced the danger of arsenic poisoning. One American plant has successfully applied the pneumatic system to the removal of the arsenic trioxide from the kitchens.

CHAPTER V

ANTIMONY

By Chung Yu Wang[1] and Guy C. Riddell[2]

History.—In point of use by man, antimony is one of the oldest of the metals. The natural sulphide was known to the people of ancient times. It was used by them as medicine and as an article of toilet for eyebrow painting by women of biblical times. A vase found at Tello, Chaldea, cast in metallic antimony discloses the fact that in about 4000 B.C. the Chaldeans knew the art of the reduction of the metal. A copper ewer and basin of the Fifth or Sixth Dynasty (about 2500–2200 B.C.), discovered in Egypt, was found covered with a thin coating of metallic antimony, thus showing that the ancient Egyptians knew something of the art of surface plating.

Basil Valentine, a German monk of the fifteenth century, and Agricola[3] wrote of liquation, precipitation, and starring of regulus. Valentine gave distinct recipes for the preparation of antimony trichloride, basic chloride, trioxide, and potassium antimonate. In the fifteenth century, antimony was in use for printers' type, and in mirrors and bells. In the sixteenth century came its use as a medicine. Of the methods now obtaining in antimony metallurgy the precipitation of metal from sulphide by iron appears in writings of the seventeenth century (Ercker), and in the eighteenth century, the roast-reduction procedure came into use. In the early 1830's came the reverberatory furnace; in 1878, direct smelting in the blast furnace; in 1844, the French volatilization process; and in 1896, electrolytic antimony first appeared in the market.

Physical Properties.—Pure antimony is a silver-white shining brittle metal. Other physical properties are: atomic weight, 121.76; atomic number, 51; specific gravity, 6.6 to 6.7; hardness, 3.0 to 3.5; specific heat, 0.05; melting point 630.5°C.; latent heat of fusion, 38.84 cal. per g.; crystallization, hexagonal.

Other allotropic forms of antimony are explosive antimony, black antimony, and yellow antimony. Explosive antimony can be produced by electrolysis, using a bath of hydrochloric acid and antimony protochloride, with antimony metal as anode and platinum foil as cathode. This form of antimony, rubbed in a mortar, loudly detonates, giving off light and heat. Black antimony is another metastable amorphous form, produced when antimony metal vapor is suddenly cooled. This form of the element is more active chemically than the ordinary metallic form, being sometimes spontaneously combustible. At 100°C. it changes gradually to the ordinary metal; at 400°C. the change is sudden.

Yellow antimony, the most unstable of the several forms of antimony, is without any metallic property and corresponds to white phosphorus and yellow arsenic. This form, obtained by introducing oxygen into antimony hydride at −90°C., is of academic interest only. It changes into black antimony above −90°C., under ordinary light.

Chemical Properties.—Antimony has three valences, three, four, and five. Its chemical properties resemble those of arsenic, and it stands close to the zinc group,

[1] Director of research, Wah Chang Smelting & Trading Co., N. Y.

[2] Consulting engineer, New York.

[3] "De re metallica," Vol. 12, 1557.

being closely similar to germanium. Antimony is but slightly oxidized at ordinary temperatures. On heating, however, the metal readily oxidizes to the trioxide. The metal is also readily oxidized by any salts that can easily give up their oxygen component, such as lead oxide and manganese peroxide. It also oxidizes in the presence of steam.

In acids, the metal is unattacked by dilute sulphuric, but forms antimonious sulphate in hot concentrated sulphuric. It is attacked by hydrochloric only when in a state of fine powder. In concentrated nitric, it is converted to the trioxide. In aqua regia it dissolves readily to form the pentachloride.

Mixed with niter and soda, antimony explodes on ignition. With alkaline nitrate and chlorate, the metal decrepitates, forming an antimoniate.

Some of the fundamental constants and chemical reactions germane to the metallurgy of antimony are now recapitulated, as follows:

Sb_2S_3 melts at 550° (Pelabon); at 540° (Wagemann); at 546° (Borgstrom)

Sb_2S_3 volatilizes, in the absence of air, between 650° and 917° (S. A. Chakhov and I. I. Slobodskai)

$Sb_2S_3 + 9O \rightarrow Sb_2O_3 + 3SO_2$; begins at 290°, rapid at 520°, and finishes at 560° (Saito); begins at 290°, if the size of the grain is 0.1 mm. in diameter, at 343° if 0.1 to 0.2 mm., and at 430° if 0.2 mm. (Friedrich); commences at 190°, energetically at 340°, and terminates at 445° (S. A. Chakhov and I. I. Slobodskai)

$Sb_2S_3 + 2Sb_2O_3 \rightarrow 6Sb + 3SO_2$; in a current of inert CO_2, gas, at 950° (W. R. Schoeller)

$x(Sb_2S_3) + y(Sb_2O_3) \rightarrow xy(Sb_4O_3S_3)$; fused under a layer of salt; at 517°

$Sb_2S_3 + Fe \rightarrow 2Sb + 3FeS$

$2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2$; H = −687,000 cal.

$Sb_2S_3 + 3H_2O \rightarrow 2Sb_2O_3 + 3H_2S$; H = +26,700 cal.

$Sb_2S_3 + 5O_2 \rightarrow Sb_2O_4 + 3SO_2$; H = −389,900 cal.

$Sb_2O_3 + O \rightarrow Sb_2O_4$; at above 445° (Chakhov and Slobodskai)

$Sb_2O_4 + O \rightarrow Sb_2O_5$; commences at 900° and finishes at 1030° (Chakhov and Slobodskai)

$3Sb_2O_5 \rightarrow Sb_6O_{13} + O_2$; at between 620 and 720° (A. Simon and E. Thaler)

$Sb_2O_6 \rightarrow Sb_2O_4 + O$; at between 750 and 800° (A. Simon and E. Thaler)

$Sb_2O_4 \rightarrow Sb_2O_3 + O$; at 930° (A. Simon and E. Thaler)

$5Sb_2O_3 + O \rightarrow 2Sb_5O_8$; at between 360 and 400° (C. T. Carnelley and J. Walker)

$2Sb_2O_3 + O \rightarrow Sb_4O_7$; at between 440 and 500° (C. T. Carnelley and J. Walker)

$Sb_2O_3 + O \rightarrow Sb_4O_7$; stable between 500 and 565° (C. T. Carnelley and J. Walker)

$Sb_2O_3 + O \rightarrow Sb_2O_4$; at between 565 and 585° (C. T. Carnelley and J. Walker)

$Sb_2O_3 + O \rightarrow Sb_2O_4$; stable at between 590 and 775° (C. T. Carnelley and J. Walker)

$2Sb_2O_3 + 3C \rightarrow 2Sb_2 + 3CO$; at red heat

$Sb_2O_4 + 4C \rightarrow 3Sb + 4CO$

$Sb_2O_3 + 3CO \rightarrow 2Sb + 3CO_2$; between 502 and 596°

$Sb_2O_3 + 6H \rightarrow Sb_2 + 3H_2O$; at red heat

$Sb_2O_3 + 3CO \rightarrow 2Sb + 3CO_2$; at 500° (Watanabe)

Ores and Deposits.—There are found in nature upward of about 112 minerals containing antimony, but only a few of them, as arranged in Table 1, can be considered as antimony ore-forming minerals.

Speaking generally, antimony lodes are simple lodes, limited in strike and depth, and belonging to the mesothermal type of deposits. Usually their sizes are irregular, pinching off rapidly. Most of the well-known deposits in various parts of the world occur, either directly or indirectly, associated with igneous rocks. They are generally granites and rocks of intermediate acidity, such as diorites, quartz-diorites, monzonites,

and quartz-monzonites. The exceptions to the general association of igneous rocks are the metasomatic replacement deposits in limestone.

TABLE 1

Class of mineral	Name of mineral	Formula	Antimony, %	Specific gravity	Mode of occurrence
Sulphide....	Stibnite	Sb_2S_3	71.4	4.52–4.62	Hypogene
Oxide......	Valentinite (rhombic)	Sb_2O_3	83.3	5–5.66	Supergene
Oxide......	Senarmontite (cubic)	Sb_2O_3	83.3	5.22–5.30	Supergene
Oxide......	Cervantite	Sb_2O_4	78.9	4.084	Supergene
Hydroxide..	Stibiconite	$Sb_2O_4.H_2O$	74.5	5.1–5.28	Supergene
Oxysulphide	Kermesite	$2Sb_2S_3.Sb_2O_3$	75.0	4.5–4.6	Supergene
Native.....	Native antimony	Sb	94–98	6.65–6.75	Hypogene
Mercury ore	Livingstonite	$HgSb_4S_7(HgS.2Sb_2S_3.S)$	53	4.81	Hypogene
Lead ore....	Jamesonite	$Pb_2Sb_2S_6$	29.4	5.5–6.0	Hypogene
Copper ore.	Tetrahedrite	$Cu_8Sb_2S_7$	24.7	4.4–5.1	Hypogene

Market and Uses.—In 1935, the United States consumed 46 per cent of the antimony of the world, Great Britain 18, Germany 13.3, France 9.4, and Italy 3.6 per cent. The average price per pound of antimony from 1908 to 1938 was 11.6 cents (minimum 5 cents, maximum 45). Ore is generally bought on an agreed price per unit (United States unit being 20 lb., British 22.4 lb.). Antimony content of the ore is generally limited to a minimum of 50 per cent. Lead, bismuth, arsenic, copper, and zinc are considered objectionable impurities and are penalized if they are present above the following percentages: lead 0.3, arsenic 0.1, copper 0.1 per cent; zinc and bismuth are considered very objectionable impurities if present in more than traces.

The trade specification for the metal or regulus is that it shall contain a minimum of 99 per cent antimony and not more than 0.3 per cent arsenic and show the usual bright "stars" on the surface.

Uses.—The principal uses of antimony, arranged in the order of magnitude of consumption, are as follows:

I. METALLURGICAL USES, in the form of alloys.

Batteries.—The largest use of antimony—normally about 30 per cent of the total United States consumption—is in the manufacture of grids in storage batteries, as used principally in automobiles. The percentage of antimony in storage-battery grids ranges from 5 to 12.

Bearings.—For bearing purposes the quantity of antimony required amounts to about 20 per cent of the annual consumption in the United States. Bearing metal is sometimes known as white metal. There are two types of white metal, the tin-base and the lead-base; the former is known commercially as "babbitt metal" or "babbitts." The genuine babbitt metal contains generally less than 10 per cent antimony and the lead-base white metal less than 15 per cent antimony.

Type Metal.—This is essentially an alloy of lead, antimony, and tin, containing up to about 30 per cent Sb.

Britannia Metal and Pewter.—Britannia metal is practically an alloy based on tin with antimony in variable proportions and smaller quantities of copper, zinc, lead, bismuth, or other metals. Pewter, an alloy of tin-antimony-copper, resembles high-grade Britannia metal.

Ammunition.—The general composition of shrapnel bullets is 12 to 15 per cent antimony, the balance is lead.

Cable Sheathings.—Cable sheathings are made of lead hardened by 0.75 to 1.00 per cent antimony.

Hard Lead.—Hard lead is simply antimonial lead. The antimonial content of the lead depends upon the use to which the metal is put, the percentage ranging from 6 per cent or lower for rolled sheets for linings and roofing to 28 per cent for special purposes, such as nozzles.

II. Chemical Uses.

Enameling.—As an opacifying agent for white enamels, antimony trioxide has almost completely replaced tin oxide, mainly because of the high price of the latter.

Pigments.—1. "Antimony white" is the trioxide of antimony which is formed as a very fine powder in the flues and dust chambers of antimony-roasting furnaces. It can be collected in this form and used without further treatment for certain paint purposes, but a specially ground and prepared oxide called Timonox is produced in England, of superior texture, opacity, and whiteness, which has become of great usefulness among pigments.

2. "Antimony black" is metallic antimony deposited electrically or chemically as a fine powder from an antimony solution and is used as a bronzing pigment for metals and plaster casts.

3. "Antimony vermilion," a red trisulphide of antimony, may be formed by precipitating an antimony salt from solution with sulphureted hydrogen. As a pigment, it is in many ways superior to red oxide of lead, red chromate of lead, or mercury vermilion.

4. "Antimony yellow" is produced by the slow oxidation of the sulphide; various shades of yellow are formed by mixing with red lead and zinc white.

5. "Antimony blue," "antimony violet," etc., are other pigments produced by mixing antimony yellow with other mineral compounds.

Rubber Vulcanizing.—Manufacturers of antimony sulphuret for use in the rubber industry customarily use the words "golden" and "crimson" to indicate pentasulphide and oxysulphide, respectively, and the word "golden-crimson" when both are present. It is still doubtful whether pure pentasulphide as such has ever been prepared. Commercial antimony pentasulphide, or "golden antimony sulphide," is generally supposed to be a mixture of antimony tetrasulphide and free sulphur ($Sb_2S_4 + S$). Whether the "crimson" product is really an oxysulphide of antimony is still doubtful. It has been considered that many of the substances described as oxysulphides of antimony are probably mixtures.

Mordants.—Tartar emetic and antimonine are the principal compounds of antimony that are used as mordants.

Ammunition.—Antimony sulphide in the form of "crudum" is used as a constituent in military and sporting arms primers and as a smoke producer for smoke screens, range-finding shells, and tracer bullets.

Fireproofing.—The largest single use of antimony today is for a new demand, the preparation of an antimony compound with chlorinated rubber or chlorinated paraffin, employing approximately 10,000 tons of the metal per year, for rendering certain essential war fabrics flameproof and fire-resistant. Materials treated with the compound quickly extinguish flames that accompany initial combustion by virtue

of an automatic chemical reaction as the compound itself is heated. Certain new fireproofing pigments of antimony base, employed in ship construction, are also increasing the war consumption.

Other Uses.—In various forms antimony is used in the manufacture of matches, medicine, fireworks, toys, etc.

The Metallurgy of Antimony.—Stibnite, Sb_2S_3, antimony sulphide, or glance, is the principal ore for the extraction of antimony. The other ores—cervantite, kermesite, valentinite, sernarmontite—are oxide ores and occur sparingly in nature. Dry methods are generally adopted for the extraction of the metal. Electrometallurgical methods have had much attention in America and Germany but have not yet found, on economic grounds, practical or extended application, except in a few rare cases. During recent years, treatment of the poor grades of the ore, especially sulphide ore,

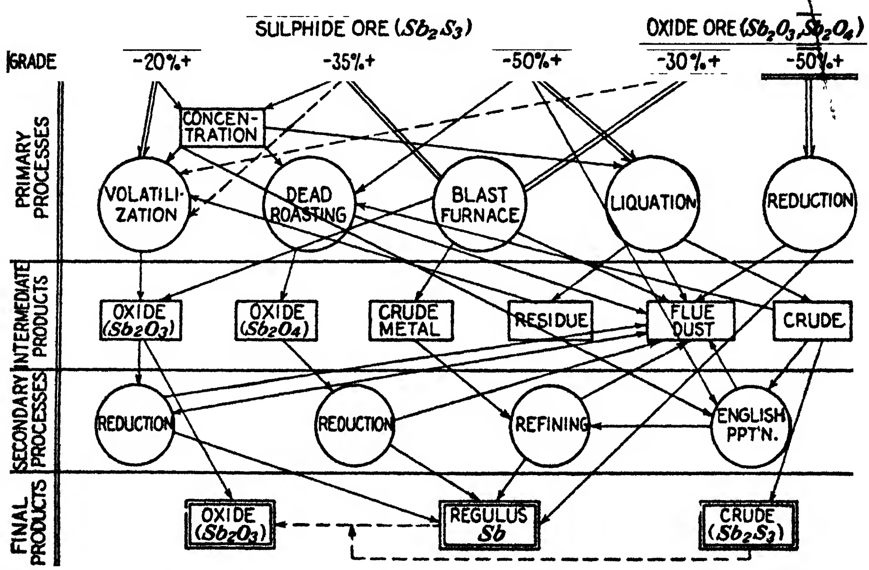


Fig. 1.—Processes for treatment of antimony ore.

by ore-dressing methods has commanded some attention and been adopted in a few cases.

The impure sulphide of antimony, resulting from the liquation process, is called "needle," "liquated," or "crude" antimony, and the refined metal itself is called antimony "regulus."

The accompaning scheme shows the different processes adopted for the treatment of various grades of antimony ores.

Liquation of Crude Antimony.—The first step in the smelting of antimony is a simple one—the process of "liquation," which produces crude or needle antimony. Ores containing about 50 per cent Sb are used in the liquation process for the production of crude. The temperature required for liquation is between 550 and 600°C. Ores to be liquated are broken to about walnut size. If the pieces are larger than this, the low heat used will not penetrate effectively, and if the size is smaller than walnut, the ore tends to pack too closely for adequate penetration. A packed charge also prevents the free escape of the fused sulphide.

Intermittent Liquation in Crucibles.—There has been developed in China a unique type of furnace for crude smelting which, in spite of the heavy loss in antimony

entailed during smelting, is simple in construction and operation, as shown in Fig. 2. The furnace is generally built in four sets of two pots each. The upper pot, which has a ½-in. hole at the bottom for the liquated product to trickle through, is the container, capable of holding a charge of 45 to 60 catties (1 catty is equivalent to about 1.3 lb.), and the bottom pot, bedded in sand or ashes, is the receiver for the liquated product. Each charge requires 2 to 4 hr. to run, and the life of the pot is generally 10 to 15 days. The liquated product is ladled into a mold, holding 16 lb. of crude. For 60 per cent Sb ore, the extraction is generally 83 per cent of the contained antimony, and for 45 per cent Sb ore, it is as low as about 64 per cent. The residue from the container contains 12½ to 30 per cent Sb, which, as will be seen later, can be extracted in a volatilization furnace.

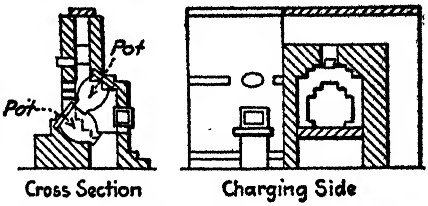


FIG. 2. -Liquation furnace and pots used in China.

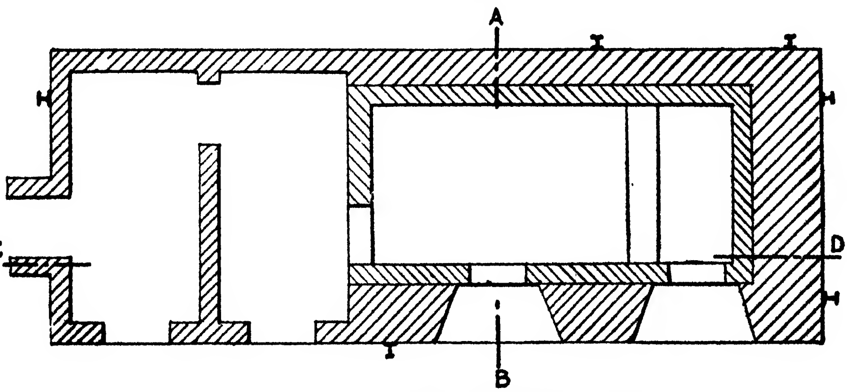
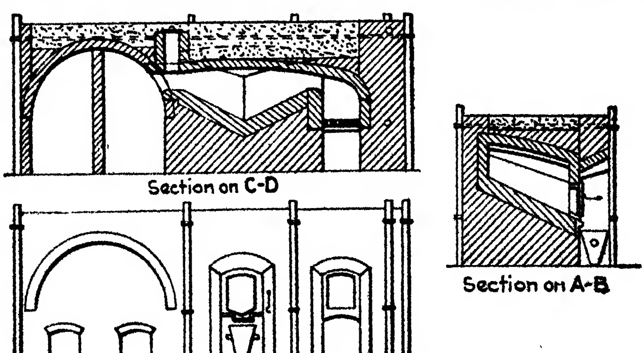


FIG. 3.—Plan of liquating reverberatory furnace.

Continuous Liquation in Reverberatory Furnaces.—The primary object of the liquation process is to free the sulphide of antimony from its associated gangue. As



FIGS. 4-5.—Elevation and cross sections of liquating reverberatory.

carried out in the old-fashioned pots, tubes, or crucibles, it is laborious, expensive, and wasteful. On the other hand, although liquation can be easily carried out in

reverberatory furnaces, the operation is attended with some difficulties. The maintenance of a reducing atmosphere, to prevent the formation of either the volatile trioxide or the stable tetroxide, is not easy to attain. While the trioxide can be partly recovered in any suitable flue or condensation apparatus, the tetroxide, found remaining in the residue, has to be considered as a loss, since it can probably be recovered only in a very high temperature upon further treatment of the residue by the volatilization process. It is regrettable that experimentation with gas-firing has never been tried out, as it is obvious that by such a method of working a reducing atmosphere can be better maintained.

Figures 3 to 5 show the construction of a liquation reverberatory furnace.

The residue from the liquation process, generally retaining about 15 to 25 per cent Sb_2S_3, may be treated in any of the volatilization furnaces to be described later.

Dead Roasting for the Preparation of the Stable Tetroxide.—Dead roasting as a process is seldom adopted, even with rich sulphide ore or crude, as the intermediate product Sb_2O_4 has no market and has to be finally reduced to the metal. Rich sulphide ores containing about 50 per cent Sb are generally treated by the liquation process for the crude or by the English precipitation method for the metal.

The oxidizing roasting of antimony ore results in either one of two products, depending on the temperature and air control—the volatile trioxide, Sb_2O_3, or the stable, nonvolatile tetroxide, Sb_2O_4.

The chemical changes taking place in the production of these two oxides are rather complicated. According to Borchers,[1] the tetroxide, Sb_2O_4, which he regarded as a salt resulting from the reaction of the pentoxide, Sb_2O_5, having an acidic character, with the trioxide, Sb_2O_3, having a basic character, is thus produced:

$$Sb_2O_3 + Sb_2O_5 = 2SbSbO_4$$

However, from a study of the temperature control of the roasting of the sulphide for the derivation of the various oxides, the authors now consider the above reaction to be apart from the facts. In a general way, when the sulphide, Sb_2S_3, is roasted, the following chemical changes take place:

Below 500°C.

$$2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2; \qquad H = +687{,}000 \tag{1}$$

Between 500 and 900°C.

$$Sb_2O_3 + O \rightarrow Sb_2O_4 \tag{2}$$

In other words, the tetroxide is derived directly from the trioxide and is not formed by the mutual reaction of the trioxide with the pentoxide. When the sulphide is heated below the temperature indicated in formula (1), the trioxide is formed with evolution of heat, amounting to 687,000 cal. This heat would instantaneously bring the particles of nascent Sb_2O_3 to temperatures well above 500°C. which then renders the reaction according to formula (2) possible, if an excess of oxygen is present.

When oxides of other metals are present, antimoniates are formed. If, also, sulphides of foreign metals are associated with the stibnite, these foreign metals are brought mostly to the form of antimoniates, instead of remaining, as they would under ordinary circumstances, as sulphates. If the proper temperature (below 500°C.) and an excess of air have been maintained, and if, in the case of rich ores, constant rabbling has been performed, the roasted mass should contain the tetroxide principally. Under ordinary working conditions, however, the product will contain antimony glass, undecomposed stibnite, and antimoniates, arsenates, and sulphates of the foreign metals present. Much attention must be paid to the regular rabbling

[1] Zinn, Wismut, Antimon, "Metallhuttenbetriebe," Vol. 4, p. 138, W. Knapp, Halle, 1924.

of the charge as the richer parts of the ore tend to liquate and to frit together. The richer the ore, the more difficult it is to roast. Toward the end of the roasting, the temperature should be raised a little, in order to complete the oxidation of any undecomposed sulphide. If carried at too high a temperature, however, the mass will frit together, and the penetration of air to the interior is prevented, and both the sulphide and oxide are volatilized.

A charge properly roasted has a reddish color while in the furnace and an ashy-gray color on cooling, and there should be no evidence of fritting in the furnace. If

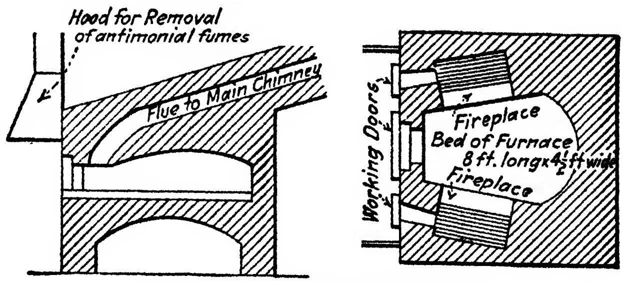


Fig. 6.—Long-bedded reverberatory.

an excess of air has not been available, the roasted product will be largely the volatile trioxide instead of the tetroxide.

The roasting of stibnite for the production of tetroxide is generally carried out in reverberatory furnaces provided with condensing apparatus. The furnaces are of two kinds: (1) small rabble furnaces (egg-shaped hearth), (2) long-bed reverberatory furnaces (similar to the hand-reverberatories of lead smelting practice). Figure 6 shows the small-type rabble furnace used in France.

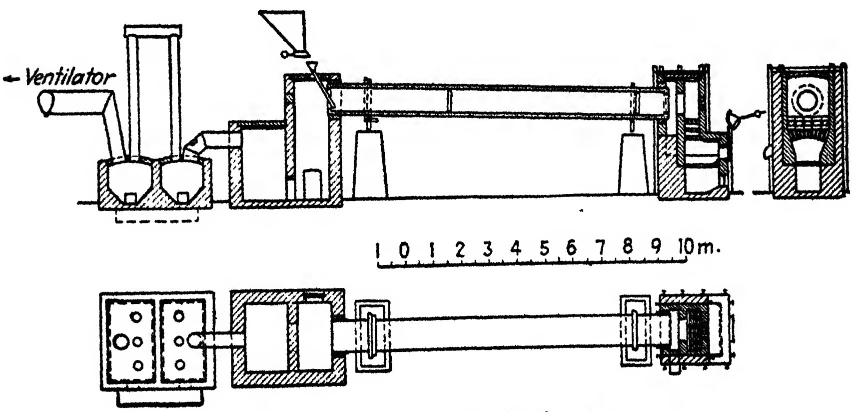


Fig. 7.—Cylindrical roasting furnace.

A rabble furnace of this type handles a charge of 5 to 6 cwt. of ground and screened ore in about 6 hr. The time required varies from 3 to 12 hr., according to the richness of the ore. During the first 2 hr. the door must be closed, but toward the end it is opened for stirring and rabbling the charge and for free admission of an excess of air. Loss of antimony in this furnace treatment varies from 4 to 8 per cent.

The long-bedded reverberatory of German, French, Italian, and American plants is about 40 ft. long by 76 in. wide. It has 8 or 10 working doors on each side and car-

ries about 1½ tons of ore, of which 6 cwt. are charged at a time. The ore works through the furnace in about 40 hr.; during the last 2 hr. before drawing, the charge is thoroughly rabbled every 5 min. and the heat is strong. Properly roasted ore has a dull grayish-yellow color. Loss of antimony in these long-hearth furnaces runs about 8 per cent.

Furnaces with a trough-shaped hearth, sloping toward one side, have been proposed, but are not in successful use, for the carrying on of both reduction and roasting at the same time. The slope of the hearth is for tapping out any accumulation of sulphide that liquates during the roasting.

The dead roasting of the ore or of the crude as carried out in reverberatory furnaces is simple, but is not entirely satisfactory, as constant and vigilant attention is required to prevent the fritting of the mass, which, when once formed, would prevent the penetration of the air to oxidize the interior of the mass. To obviate such diffi-

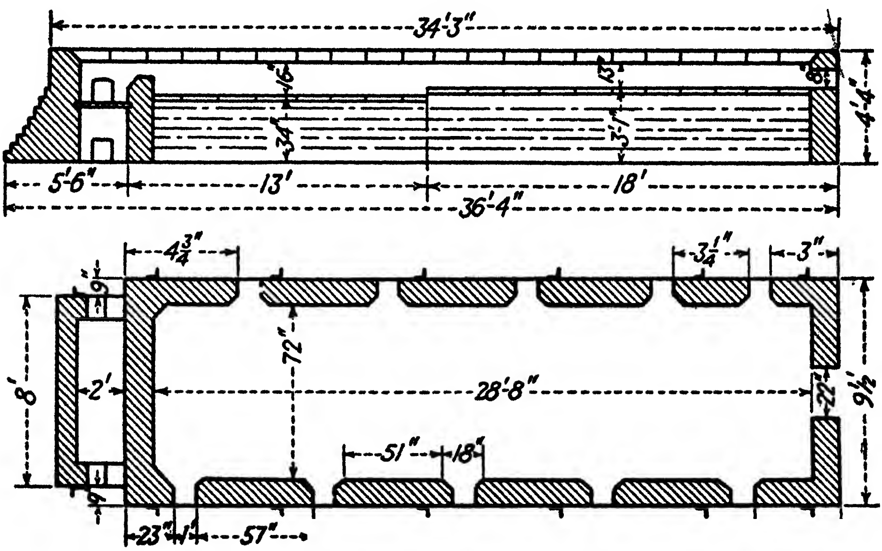


FIG. 8.—Reverberatory roasting furnace.

culty as well as efficiently to oxidize the charge to the stable tetroxide without the expenditure of much labor, A. Lissner and E. Eichelter[1] have made use of a cylindrical rotary furnace of 12 to 20 m. in length, with some degree of success, as illustrated in Fig. 7. Such a furnace can be fired with flaming coal or gas, preferably with the latter. The draught can be regulated with a ventilator, while any volatile oxide formed can be condensed in any suitable flue or condensation apparatus.

At the Wah Chang Mining & Smelting Co., Changsha, China, the crude was first ground into powder in a Chilean mill and was then fed into a reverberatory furnace, as shown in Fig. 8, which could dead-roast 2000 lb. (906 kg.) of crude per 24 hr. with a consumption of 700 lb. (317 kg.) of coal. Two workmen were required per furnace per shift of 12 hr.

Volatilization Roasting for the Trioxide.—Practically all the shaft furnaces for the volatilization process are based on the same principle. The ideal ore for treatment

[1] The Use of a Rotary Furnace for the Roasting of Rich Antimony Ore. *Metall u. Erz.*, Vol. 19, p. 373, 1922.

in such furnaces is one containing 15 to 25 per cent antimony; ore above 40 per cent Sb would partly volatilize and partly liquate, and part of the liquated product would combine with the volatilized trioxide to form an oxysulphide compound, commonly known as "antimony glass," which causes fritting at the lower zone of the furnace. Even with ore containing 30 to 35 per cent Sb, some fritting might occur, necessitating the maintenance of the furnace at a higher temperature than necessary for poorer ores. Hence the paradox: the richer the ore, the higher the percentage of coke required for the charge. It is possible to volatilize an ore of about 20 per cent with 4 to 6 per cent charcoal, the temperature being thus kept at low red-heat. On the other hand, with liquation residue which ranges from 15 to 25 per cent, the problem is different. Here we have a material that disintegrates and packs at a very low red heat, thus partially blocking up the furnace and preventing free passage of the air upward. To remedy this, some works use a forced draft, while others use an excess of coke, amounting to 30 to 50 per cent of the charge, thus increasing the porosity of the charge. One can frequently tell when the furnace is blocked or when the suction fan is choked with the trioxide, especially if water is introduced into it, by observing the appearance of a reddish tint in the issuing trioxide fume, which would be white with the furnace working under normal conditions. A plausible explanation for the appearance of this reddish tint in the otherwise white trioxide is found in the formation of the compounds Sb_2S_2O, $Sb_2O_3.2Sb_2S_3$, $Sb_2O_3.2Sb_2S_3.4H_2O$, or $Sb_2S_3.2H_2O$. Some sulphide particles from lack of free oxygen might be volatilized as such at temperatures above 650°C., taking up the moisture still in the ore. Another fact, which seems to substantiate such an explanation, is that whenever a new furnace, or one that has been standing idle for some time, is started the trioxide fume is frequently colored red at the commencement and continues so until the furnace is well under way. The explanation here is that there must be present a certain amount of moisture in the furnace, and it is this moisture that is taken up by the volatilized sulphide to form the above-mentioned red hydrated sulphide. In fact, an analysis of this pinkish oxide sometimes shows the presence of 5 to 6 per cent S.

It is impossible to maintain uniform temperatures throughout the furnace shaft. The bottom part of the furnace, where the burned-out ore is ready to discharge, is cooled by the incoming air, while the top part is also comparatively cool. The central part thus localizes a hot zone of reaction where fusion of the silicate-forming minerals of the gangue and in the coke causes frequent trouble.

While Otto Barth[1] states that the volatile trioxide exists only below 700° and above 1100°, our experience indicates that antimony sulphide, when roasted under properly restricted admission of air, changes to the volatile trioxide below 445 or 560° and above 930°, while between the two limits, the oxide exists only as the stable tetroxide. In practice, the stable tetroxide may be considered to exist between 500 and 1000°. It is thus obvious that proper control of temperature is important for the successful operation of the volatilization process.

The many advantages of this method of treating low-grade antimony ores have brought it into general favor, and it is extensively used in one form or another in France, China, Yugoslavia, and elsewhere. These advantages are: (1) When the ores contain precious metals these are found in the residues after volatilization. (2) Barring dressing the ores, it is the only method really suited to low-grade ores. (3) With different devices for condensation, the loss of antimony can be greatly lessened. (4) Less fuel is required, as the sulphur in the ore can be utilized as fuel. (5) The condensed trioxide can be reduced to metallic antimony, or it can be marketed as white oxide to make paint, enamels, etc.

[1] "Die Metallverflüchtigungsverfahren mit besonderer Berücksichtigung der Herstellung von Zinkoxyd," p. 65, W. Knapp, Halle, 1935.

Of the various modifications that have been developed in the volatilization method of producing antimony trioxide, the following important ones are described.

Herrenschmidt Process.—Figure 9*b* is a longitudinal section and view of Herrenschmidt's finally perfected equipment (1908). Figure 9*a* is a cross section of a roasting furnace along *AB*. Figure 9*c* is a longitudinal section along *JY*.

The broken ore, carrying 10 to 20 per cent antimony, is charged, mixed with 4 to 8 per cent charcoal, into the roasting furnace *a* the bottom of which is formed by horizontal iron bars *b*. The volatile antimony trioxide is deposited on condensation pipes *e*, in the condensing chambers *d*, under suction from the two fans *h*. The last trace of the uncondensed oxide is caught by the water coming from the coke tower *i*, at the top of which are the water pipe *j* and the seesaw water distributor *k*. The roasting furnace is built partly of bricks, partly of cast metal. The condensing chambers are of cast iron, and the coke tower of wood. Each condensing chamber is 1 m. long.

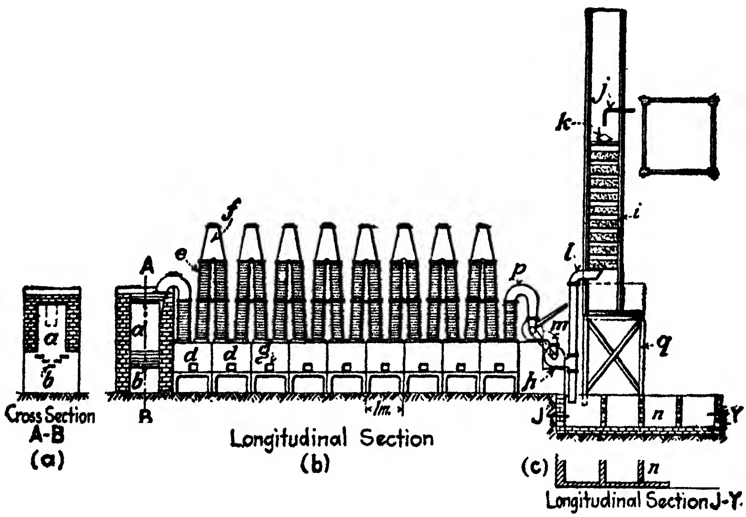


FIG. 9.—Perfected Herrenschmidt volatilization and condensation apparatus.

With mine-run ores, carrying 10 to 15 per cent antimony, 6 tons can be treated in 24 hr., with a fuel consumption of 4 to 5 per cent gas coke or 6 to 7 per cent charcoal. With ore containing 18 to 20 per cent antimony, 4½ tons per 24 hr. can be treated with a fuel burden of 5 to 6 per cent gas coke or 7 to 8 per cent charcoal. Each unit employs four workmen per 24 hr., and the fans and pump require 3 hp.

Gas coke gives better results, if obtainable, but most of this antimony work is done in out-of-the-way places, where charcoal is cheaper.

The size of the ore treated is 1 to 4 cm. Ore dust must be separated out, and, if present in large quantity, must be briquetted with 7 or 8 per cent clay into balls of proper size and charged along with the ore. The working of the furnace proceeds as follows:

A charge of old scoria is placed on the grates up to a height of about 10 cm. above the uppermost bar; and wood and charcoal are put in to a height of another 10 cm. As soon as the fuel is lighted and burning freely, another charge of 300 kg. of scoria, mixed with 6 per cent charcoal, is put in. Finally, when the furnace is up almost to full heat, an ore charge of 50 kg., mixed with 2 kg. of charcoal, is put in, and this is continued until the furnace is full to within 30 cm. from the mouth. The same charge

is repeated every 12 to 14 min., according to the rate of revolution of the ventilating fans—which is 1200 to 1400 r.p.m.—and the scoria is discharged accordingly.

The temperature of roasting, for trioxide production, should not be over 500°C. About 30 cu. m. of water per day are required for one apparatus.

The loss of antimony in the Herrenschmidt apparatus is variable, approximating 10 per cent; the skill of the laborer is all-important. By manipulation and spreading of ore and fuel so that the ore is thoroughly burned and the antimony contents fully volatilized, the percentage of fuel can at times be cut down to about 3 per cent, and the yield of oxide can be increased to 95 per cent.

The Wah Chang Mining & Smelting Co.'s plants in China, for several years the leading producers of antimony, used about 15 per cent charcoal on ore running 20 to 35 per cent antimony; if the charge consisted of liquation residue, the charcoal required amounted to 20 to 22 per cent for coarse and 24 per cent for fine. The scoria discharged from the shaft furnaces generally carried about 3.5 per cent antimony from ore charges, and 4.5 per cent antimony from the liquation residue charge.

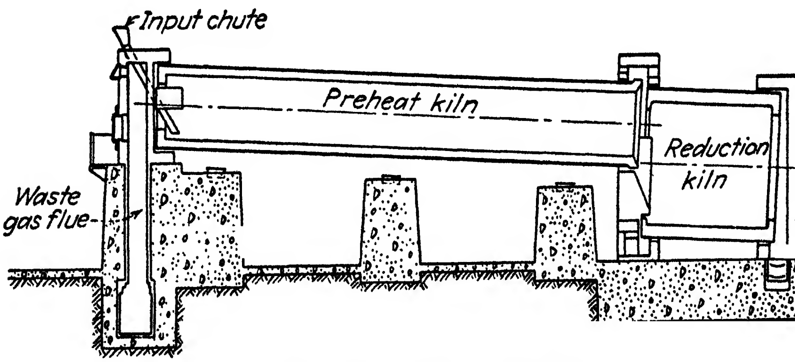


Fig. 10.—The Follsain furnace.

The Follsain Furnace.[1]—In 1926, Friedr. Krupp-Grusonwerk A. G. patented the so-called Waelz process for the treatment of zinc, lead, cadmium, arsenic, antimony, bismuth, and tin ores. This process has been adopted by the Podringi Consolidated Mines Ltd., in their antimony smelting work at Krupanj, Yugoslavia. In principle, the Waelz process is somewhat similar to the Follsain process.

The Follsain furnace as illustrated by the diagrammatic drawing (Fig. 10) is a revolving furnace. The preheating kiln is approximately 30 ft. long and 36 in. internal diameter, and the secondary or carbon combustion zone is about 7 or 8 ft. long by 6 or 7 ft. diameter. The air for combustion is heated in an air heater to about 750°C. The waste gases carrying the antimony trioxide fume leave the kiln at a temperature of 230 to 250°C. and are then passed to a Cottrell electric precipitation plant for the recovery of the antimony trioxide. Fuel consumption is 25 to 30 per cent of the weight of ore charged. Power consumption is 5½ to 6 kw.-hr. per ton of ore treated. For the treatment of, say, 20 tons of 20 per cent Sb ore per day, two revolving furnaces, as illustrated, are required.

Antimony Smelting at Cortis Rosas (Ballao), Sardinia.[2]—It is interesting to note that in this smelter a converter has been adopted for the volatilization process. It seems that this converter is an adoption of the "convertisseur" apparatus patented

[1] Private information from Follsain Syndicate Ltd. (London).

[2] Sul trattamento dei minerali di antimonio in Sardegna, *Industria*, Vol. 32, pp. 437–438, July 31, 1918.

by Collin[1] in France. The converter is composed of two parts, as shown in Fig. 11; the bottom part, which is hemispherical in shape and can be revolved horizontally on two bearings for the discharging of its contents, and the top part, which acts as a hood. Compressed air enters from the bottom, while the volatile fume is drawn from the top of the hood by means of an aspirator. This method is specially adaptable to the treatment of fine ore, especially ore of a calcareous nature, which if treated in a shaft furnace, would render the operation difficult and troublesome.

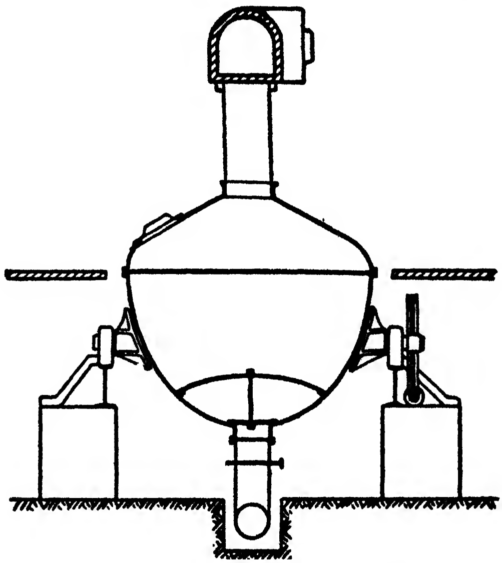


FIG. 11.—Cortis Rosas converter.

The Blast Roaster.[2]—The blast roaster as shown in Fig. 12 is intended to be an improvement of the usual shaft furnace for treating low-grade antimony ores. It is in principle a modified form of water-seal gas producer, employing mechanical charging and discharging devices. The blower delivers air to an annular space or wind box around the furnace, before entering the latter through the grate. The coke consumption for the roasting proper will be lower than that for an ordinary shaft furnace, as the air is preheated.

The blast roaster differs from the ordinary shaft roasting furnace mainly in that it uses air under pressure instead of under suction. Since the product of roasting is volatile antimony trioxide, it is obvious that an upward movement of air under pressure through the ore bed would be more positive in assisting volatilization of the trioxide besides furnishing the necessary oxygen for chemical reactions. It also uses a principle of blast roasting in its progressive roasting action through the ore bed, but it differs from the general practice of blast roasting in that the sulphur content of the whole charge is low, only about 7.17 per cent (assuming 20 per cent Sb ore grade and 10 per cent coke consumption) as against 12 to 14 per cent for lead and zinc ores in blast roasting; therefore there will be no incipient fusion of the ore particles, which is an essential factor of the latter process. Although it is like a gas producer in both

[1] Convertisseur pour la séparation des métaux fixes et volatils dans les minéraux complexes, Marcel Collin, French patent 428708, Sept. 6, 1911.

[2] Private communication from C. C. Chao, metallurgist of the National Resources Commission, China.

construction and operation, there will be no reducing effect because (1) the coke in the charge is isolated by the excessive gangue of ore and (2) the blast delivered will be more than sufficient for the theoretical roasting and combustion, thus ensuring an oxidizing atmosphere throughout the ore column. It also differs from the blast-furnace smelting in not slagging the gangue with fluxes and in treating a low grade of ore. Thus there will be no self-reduction effect of stibnite.

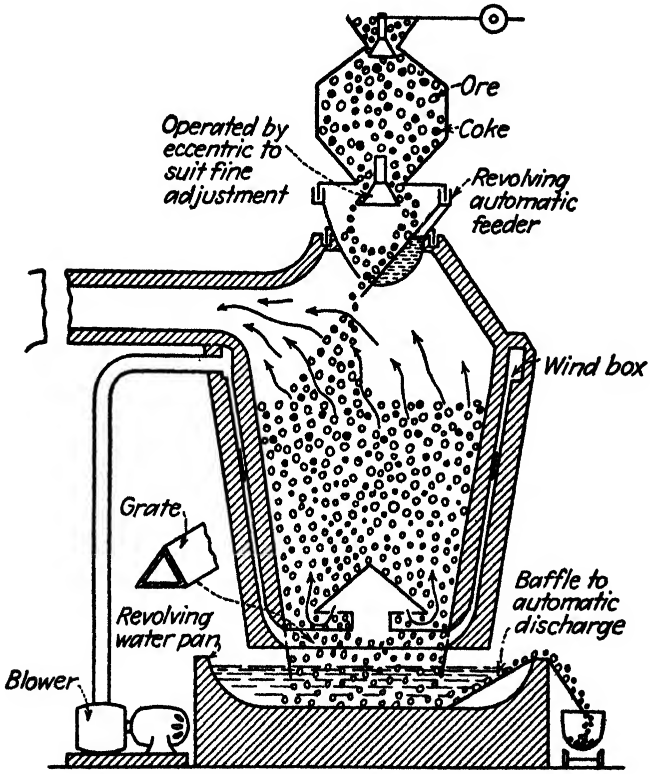


FIG. 12.—Blast roaster.

Other Processes for Preparation of the Trioxide.—There are perhaps a dozen processes for the preparation of the volatile trioxide, which at different periods, in France, Italy, and Germany, have had some prestige. In all of them, the principle of roasting, volatilizing, and condensation of the oxide is, of course, the same; differences exist merely in the forms of furnaces, condensers, and methods of collecting the oxide.

In the Chatillon process, which has been employed on a large scale in France, the furnace consists of two double cupolas terminating in a common flue from which the volatilized oxides are led to water-cooled condensing chambers made of sheet iron. The upper cupolas are charged with alternate layers of fuel and ore, and as the liquated sulphide melts and falls through to the lower cupola, it meets an upward current of hot air that converts it into the trioxide, Sb_2O_3. Before leaving the plant the gases are reduced to a temperature of 100°C., and passed through a baghouse. The sublimate obtained contains 98 to 99 per cent antimony trioxide.

The Blast Furnace.—The blast furnace can be operated as a producer of both antimony trioxide and metal at the same time. Treatment of this subject will be taken up under the next heading.

Pigment Trioxide.—The trioxide, as produced in the treatment of the ore by the volatilization process, is generally impure and coarse and hence is not suitable for pigment purposes, although it may be used as an opacifying agent for white enamels.

The following processes may be adopted for the production of pigment trioxide.

The process adopted by the antimony smelter at Costerfield, Victoria, Australia, was as follows:[1] "The furnace was a small circular cupola with four tuyères at the top of the hearth and two more admitting air to the top of the charge above the feed door. The condensing section of this plant consisted of a firebrick and red brick chamber, a cyclone, and baghouse with a centrifugal fan placed in the circuit at the intake of the baghouse. The oxide with a small amount of reduction slag from the starring furnace was charged into the furnace on a bed of burning coke where it soon volatilized. The cooling of this oxide took place very rapidly so that it was deposited mostly in the amorphous form as very small spheres. A small amount of crystalline oxide was also collected at the cyclone. The baghouse product was the most suitable as a pigment on account of the fine state of division of the particles, approximately 0.0025 mm. in diameter, and its spherical form and whiteness."

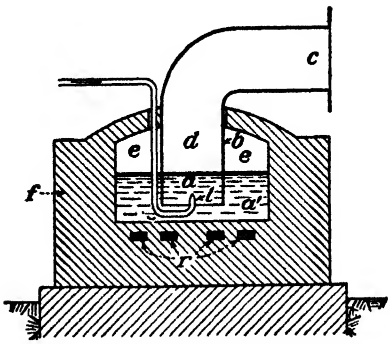


Fig. 13.—Germot trioxide furnace.

Antonin Germot[2] proposes the following method of manufacturing antimony trioxide: A furnace *f* (Fig. 13) in masonry, heated to the appropriate temperature by any known means, preference being given to electrical resistances *r*, receives an inverted bell *b*, provided with one or more blowing-in tubes *l*, which open at the lower part of the furnace, the orifices of the tubes being disposed above the lower edge of the bell. The bell *b*, dipping into the metallic bath *a*, thus forms a closed chamber *d* which contains only the air or oxygen blown in by tubes *t*. The air oxidizes the molten metallic antimony to Sb_2O_3 in the state of clouds of impalpable powder, which is discharged through the neck *c* and collects in any settling chambers. Fresh antimony in lumps is added to the bath from time to time.

Jean Joseph Listrat[3] proposes to treat antimony sulphide ore, for liquation and volatilization as antimony trioxide, in one operation. However, it has been found in practice that antimony crude alone forms the best charge for such treatment. The apparatus consists of a furnace 10 (Fig. 14) having three cupola chambers 11, 12, and 13. The central chamber 12 communicates with any receiving apparatus for the fumes of oxide given off, and the end chambers 11 and 13 are directly connected to any condensation apparatus. Air is blown into these chambers through inclined pipes 14. Antimony ore or antimony sulphide is introduced into the central cupola chamber 12. Any suitable source of external heat is used for originally heating the central chamber after which, when the process gets under way, the exothermic reactions will provide all the necessary heat. The gangue from the ore charged may be taken off at proper intervals through the taphole. The purest oxide obtained is from chambers 11 and 13.

[1] McLean, *Chem. Eng. Mining Rev.*, Dec. 6, 1926, pp. 94–95.
[2] British patent 203519 (1922); U. S. patent, 1504685, Aug. 12, 1924.
[3] U. S. patent 1873774, Aug. 23, 1932.

Antimony oxide pigment,[1] known in England under the trade name Timonox, is now manufactured in France by a patented process,[2] by which metallic antimony obtained by dissociating the trisulphide at a high temperature, probably above 1020°C., is subsequently oxidized to the trioxide. Traces of sulphur trioxide in the antimony oxide are removed by vigorous washing in lime water, agitated by compressed air.

The main points of the process[3] as patented by the Deutsche Schmelz-u.-Raffinierwerke A. G. for the manufacture of antimony oxide for pigment purposes are: (1) the air for oxidizing the metal is diluted by nitrogen, carbon dioxide, combustion gases, principally by exhaust gases; (2) the antimony used is directly heated by burning gas which plays on the surface of the metal; (3) the oxygen content of the flame is so adjusted that the antimony oxide obtained is amorphous; (4) the temperature of the antimony bath must be brought to about 1000°C.

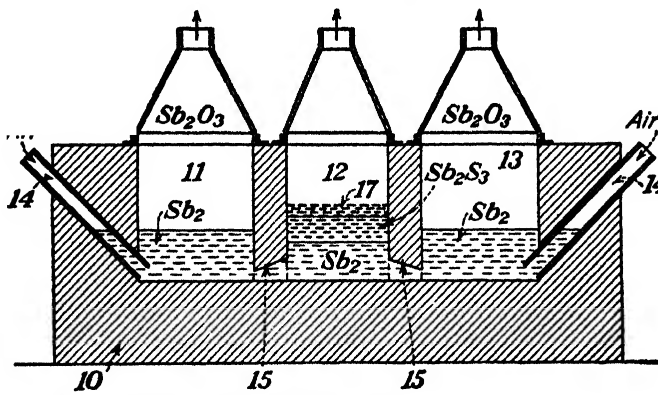


FIG. 14.—Listrat antimony furnace.

Methods for the Production of Metallic Antimony.—The last phase in the metallurgy of antimony is the production and refining of metallic antimony. Unrefined antimony metal is sometimes called crude antimony, but the metal is never marketed in this form; the name would be confused with liquated sulphide which is commonly called crude antimony, or more correctly antimony *crudum*. Antimony metal may be obtained from (1) the oxides (trioxide or tetroxide), (2) from antimony *crudum*, or (3) by direct smelting of antimony ores. Of these methods, the bulk of the world's antimony, up to the present time, has been produced by the first two mentioned.

The direct smelting of metal from its ores was receiving a great deal of attention, however, in the United States (San Pedro), Mexico (Wadley), and England during the period just preceding 1918, and in earlier years at Banya in Bohemia, and some very successful results were being achieved. It is not overstating the case to say that the operators of the blast furnaces engaged in this direct smelting had, prior to the great metal depression, already accomplished such progress in the normal blast-furnace reduction of antimony ores as to indicate the possibility of a complete reconstruction of the practice of antimony metallurgy. In fact, at the present time, at the Laredo plant in Texas, at a plant near Mexico City, Mexico, and at a plant in France, blast-furnace practice is adopted. It is well demonstrated that the blast furnace is the best appliance for a certain class of antimony ores—those containing

[1] *Chem. Trade Jour.*, Vol. 83, pp. 337–338, 363–364, Oct. 19, 26, 1928.
[2] *Metall u. Erz.*, Vol. 29, pp. 105–113, March, 1932.
[3] British patent 345034, Mar. 19, 1931.

about 25 to 40 per cent of metal. These are too high to be best suited for roasting and are yet too poor for liquation or direct precipitation smelting, and for their treatment, as well as for by-products of the same richness, the blast furnace offers undoubtedly the best method.

Under the methods that have, in general, so far prevailed, reduction of the oxides is carried out either in reverberatory furnaces, in water-jacketed or blast furnaces, or in crucibles. In reducing the oxide, care must be taken to control volatilization and to keep any unaltered sulphide out of the mass of metal. A fusible slag is utilized, which forms a cover preventing volatilization and which also dissolves any metallic sulphides left. This slag, composed of soda, potash, and Glauber's salt, acts as a refining agent, carrying off most of the impurities that may be in the oxides. On ores carrying low percentages of antimony, the volatilization and reduction processes are used, because they are considered to be the cheapest of all methods and produce a very pure metal.

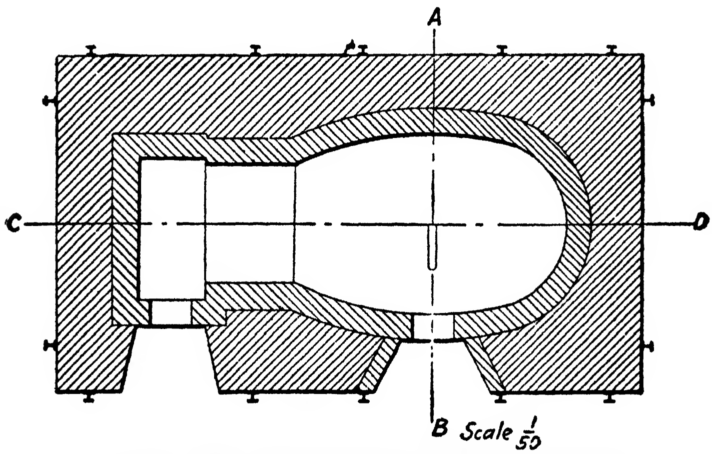
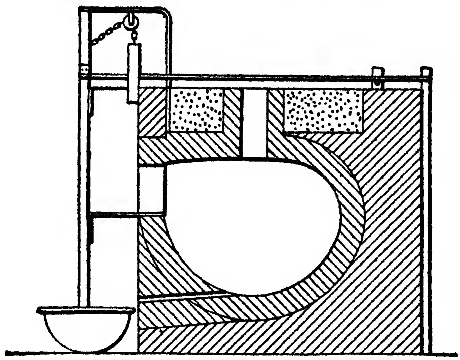


FIG. 15.—Plan of reverberatory for reduction method.

Reduction of Oxides in Reverberatory Furnaces.—Of the several reduction methods, the reverberatory is simple and easy to control, but it is attended by heavy loss of antimony and is, therefore, used for rich ores and cheap fuel. Loss of metal generally runs from 12 to 20 per cent and may be as high as 30 to 40 per cent with careless working. In France, Austria, and New Jersey, the reverberatories used have been of approximately the following dimensions: hearth, egg-shaped, length about 8 ft.; width in center, 5 ft. 3 in.; width at fire bridge, 3 ft. 4 in.; height of fire bridge, 1 ft. 4 in.; width between top of fire bridge and roof, 1 ft.; maximum height of roof over bed, 3 ft. 3 in.; opening for charging, 1 ft. 4 in. wide. At the deepest part of the bed is a hole through which the metal is tapped. An 8-in. flue leads into condensing chambers about 400 ft. long. The antimonial vapor passes into these chambers and is deposited there. Figures 15, 16, and 17 show the type of furnace used.

The precipitate recovered in the condensing chambers contains up to 50 per cent antimony. The furnace charge consists of about 500 lb. of roasted ore, oxidized ores, oxides, liquation residues, flue dust, etc., together with about 100 lb. of flux composed of salt, soda, about 70 lb. of ground charcoal, and sometimes a small quantity of Glauber's salt. It is also found to be good practice to remelt about 300 lb. of slag from previous charges. The flux is charged into the furnace first, and when it is melted down and all boiling or agitation of its surface has ceased, the other materials

are charged into the furnace, about 40 lb. every 15 or 20 min. The charge is then well stirred, and the scum produced is drawn off. After the last charge has been put in, the temperature of the furnace is raised and kept up until the process is completed. During the smelting, the charcoal acts as a reducing agent, robbing the antimony of its oxygen, while part of the soda combines with the sulphur, and the remainder helps to form a slag with the gangue. Any other metals present are carried into the slag

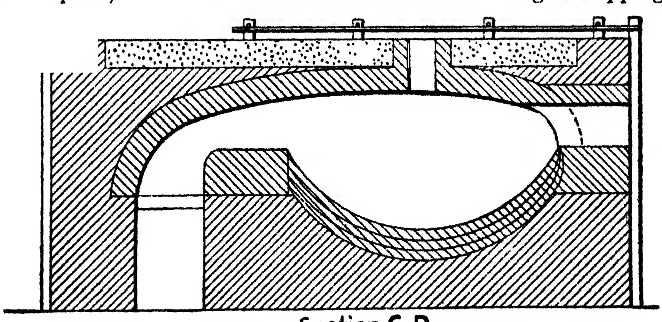


Section A-B

Fig. 16.—Section of reduction reverberatory.

as sulphides by the action of the sulphide of soda which is produced through the reduction of the Glauber's salt by the charcoal. Common salt serves the same purpose by carrying foreign metals into the slag as chlorides.

The fuel consumption is somewhere between 5 and 6 cwt. per charge, and the loss is usually about 14 to 15 per cent. When considerable antimony sulphide is present, a little iron or iron slag may be added to assist in reducing the sulphide. When the smelting is complete, the metal is drawn off into molds through a tapping hole, and



Section C-D

Fig. 17.—Section of reduction reverberatory.

during the cooling in the mold, care must be taken to have it completely covered over with slag. When the metal solidifies, the slag is knocked off by hammering.

The charge is thoroughly rabbled after about 6 hr. in the furnace, and the metal separates out from the slag which is skimmed out, and is soon ready for tapping into molds. The "starring" of the regulus is done in the mold. A purifying mixture, composed of 6 parts of carbonate of soda and 4 parts of antimony trioxide, is melted down in a small chamber at one end of the reverberatory furnace or in the furnace itself after the slag is skimmed away. When the metal is ready to be tapped, some of this molten mixture is poured into the molds to be used. The regulus is then run

into these molds, and the purifying mixture, being lighter, immediately comes to the top, forming a cover over the regulus. When the metal solidifies, any of the mixture remaining on top is removed by hammering.

Reduction of Oxides in Water-jacketed Blast Furnace.—In California and Mexico, blast-furnace smelting of antimony ores has been brought to a high degree of efficiency. The manipulation of the furnace and charge has much in common with the ordinary practice of the lead blast furnace.

Roasted ore, briquetted flue dust and oxides, and smaller amounts of unroasted stibnite, together with siliceous waste for slag-forming material, make up the charge. Recovery of antimony runs 95 to 98 per cent, slags carrying about 1 per cent, sometimes running as low as 0.25 per cent, of antimony.

The Cookson plant, at Wadley, Mexico, handled ores of a refractory nature and of comparatively low grade. The antimony content varied from 25 to 40 per cent. The ores at Wadley were, in the main, oxidized, between 80 and 90 per cent of the antimony being present as oxide, the remainder being sulphide. The gangue was siliceous and calcareous. On account of the refractory nature of the ores and their oxidized condition, the comparatively simple methods of smelting adopted in China were not satisfactory, nor could the usual English methods be employed. They have, however, proved amenable to blast-furnace treatment. The plant was somewhat elaborate and costly, in comparison with the reverberatory methods, but excellent smelting results were obtained. The plant was seldom in operation with antimony below 12 cents per lb., c.i.f. New York.

The ores, after rough concentration, were smelted in rectangular water-jacketed blast furnaces, similar to those employed in smelting lead ores. Limestone and iron ore were used as fluxes and coke as the reducing agent. The blast furnaces were some 28 ft. high, 5 × 3 ft. hearth area, and were blown by compressors delivering air at a pressure of 2 to 3 in. of mercury. A forehearth was provided to separate the metal from the slag. Owing to the high temperature attained in the blast furnace, and to the volatility of antimony, very efficient baghouses were necessary to deal with the fume carried over in the blast-furnace gases. The fume was briquetted and worked off with the ore in the blast furnaces. By running a highly siliceous slag, the antimony content of the slag was kept down to about 1 per cent.

The antimony obtained as above, generally termed "singles," contained 5 to 7 per cent iron and 1 to 2 per cent sulphur. Deleterious impurities were practically absent, as the ores, apart from their low grade, were very pure.

The iron and sulphur in the singles were removed by submitting the metal to the "doubling" process, which consisted of a combination of liquation and fusion under alkaline fluxes in reverberatory furnaces. The resulting "doubles" were further refined and starred by Cookson & Co.'s special starring process, the resulting "Star" antimony being of high quality and guaranteed 99.6 per cent purity.

Reduction of Oxides in Crucibles.—This method of reduction is now seldom used. The use of crucibles and pot furnaces precludes the working of large charges. Fuel consumption is high, and each pot has a life of only seven or eight charges.

Extraction of Metal from Crude.—Antimony crude or antimony "needle" is frequently marketed and used for various purposes, such as for vulcanizing rubber, matchmaking, and for ammunition manufacture. As the market for crude is limited, it is necessary to convert the greater part of it into antimony regulus. This may be done in one of two different ways: (1) conversion of the sulphide into antimony oxides, and then reducing the oxides in reverberatory furnaces; (2) direct smelting of the sulphide to metal, iron being added as the reducing agent.

English Precipitation Method.—In China, the English precipitation has been found too inconvenient and costly to compete successfully with the oxidizing methods,

and the latter have become the accepted mode of treatment for crude in that field. In England, Hungary, Japan, and Mexico, however, the precipitation method remains in vogue, rich ore or antimony *crudum* being directly reduced to metal by crucible fusion with metallic iron. The fundamental principle involved in this method is the greater affinity of sulphur for iron than for antimony. In the precipitation process, iron is used to decompose the sulphide of antimony to give sulphide of iron and antimony as in the equation

$$Sb_2S_3 + Fe_3 = 2Sb + 3FeS$$

Iron sulphide is formed, even at a comparatively low temperature, the antimony being separated out in the metallic state. The high specific gravity of the iron sulphide makes it difficult to separate the antimony from the iron sulphide, and it is necessary to add sodium sulphate and carbon in order to produce sodium sulphide, which, combining with the iron sulphide, forms a fusible matte of low specific gravity. In England, instead of sodium sulphate and carbon, common salt is used. The iron is usually added in the form of turnings, shavings, or tin-plate cuttings. The proportion of iron must be carefully controlled, for if sulphides of lead and arsenic are present, they will be reduced by any excess of iron not taken up by the stibnite and will enter into the antimony metal as impurities.

It is found in practice that the theoretical amount of iron required for desulphurizing the stibnite is not sufficient, owing to the fact that part of the iron is taken up in decomposing the sodium sulphate.

Losses of antimony in the precipitation method occur from both volatilization and slagging, running 10 per cent, or over. Ordinarily, the process is carried out in crucible furnaces. Shaft and reverberatory furnaces are used in some cases, but the metal losses are much greater in the latter furnaces.

The English process proceeds as follows: The stibnite is reduced by metallic iron in crucibles in a long reverberatory furnace. Dimensions of the furnace are: length, 54 ft.; width (inside), 7 ft. 4 in. The bed is covered by a low arch which springs almost from the surface of the ground, the bed itself being below ground level. It is heated by a fireplace at each end, a common flue taking off from the middle of the furnace floor. The sides and roof of the furnace are covered with cast-iron plates.

The crucibles are lowered into place through 14-in. circular holes in the arch, 42 holes (21 on each side) being provided. The pair of crucibles nearest the fireplaces at each end is kept for "starring," or refining, the crude metal. Each crucible takes a charge of ore (hazelnut size), 42 lb.; iron, 16 lb.; common salt, 4 lb.; skimmings (from the doubling operation), or slag from previous smelting, 1 lb.

Tinned scrap is preferred; for insertion into the crucible it is pounded into a round ball, large enough to fit the top of the crucible. The balance of the iron required is in the form of turnings or borings, which are mixed with the ore, together with the salt. The mixture is dropped into the crucible through a funnel; the furnace hole is then closed for half an hour, when the crucible is examined. The salt used assists the separation of the slag and tends to promote the fusion of the siliceous material. On an average, four meltings are made in each crucible per 12 hr.; the richer the ore, the shorter is the time required.

The crucibles are made of a mixture of graphite and fire clay and are generally 20 in. high and 11 in. across the mouth. The crucible, dry, weighs 42 lb., of which approximately 36 lb. is fire clay and 6 lb. graphite.

A mold, conical in shape, is placed opposite each crucible. The metal obtained is known as "singles," and contains about 91.6 per cent antimony, 7.3 per cent iron, 0.8 per cent sulphur, and 0.3 per cent insoluble matter.

The singles are next purified by fusion with a small amount of liquated sulphide of antimony, to remove the iron remaining in the metal. The charge for this second, or "doubling," process is: singles (broken small), 84 lb.; antimony crude, 7 lb.; salt, 4 lb. *The fused mass is stirred occasionally with an iron rod, the time required for one* charge being about 1½ hr. When fusion is complete, the slag and matte are ladled off with an iron spoon and the contents of the crucible poured into the molds used in the previous fusion; the matte and skimmings are added to subsequent ore smeltings. The metal thus obtained is known as "star bowls," and contains 99.0 to 99.53 per cent antimony, 0.18 per cent iron, and 0.16 per cent sulphur.[1]

The effectiveness of this second liquation can be understood when it is remembered that in such an alloy of antimony and iron intermetallic compounds are present. One of these, with the chemical formula Fe_3Sb_2, has a freezing point of 1016°C., and another ($FeSb_2$), which forms from Fe_3Sb_2 and liquid, crystallizes out at 730°C. The melting point of pure antimony is 630°C. Hence, in the heating up of this alloy, the antimony first melts and the antimony-iron compounds tend to separate and rise to the surface. These are then "taken up" by the slag and removed from the bath of metal under purification.

The presence of sulphur, due to the excess of crude used, is indicated by the crystalline pattern that forms on the surface of the metal being covered with small glistening patches, the latter being known as "flouring." In order to remove this sulphur, another fusion is necessary.

Starring.—The custom of the trade is to demand antimony that is "starred," or crystallized, on the upper surface, and it is at this stage that this "star" is obtained. These two results are accomplished by melting the metal with what is known as the "antimony flux," a substance that is often difficult to obtain, in proper composition, at first. This flux is prepared by rule-of-thumb method, about as follows: 3 parts of ordinary potash are melted in a crucible, and 2 parts of ground liquated sulphide are mixed in. When fusion has become quiet, the mixture is poured out and tried on a small scale to find out whether it yields a good star. If the star is satisfactory, the ingot of metal obtained is then broken and the metal examined in order to determine whether it is free from sulphur. If, however, a good star is not obtained, the flux is remelted, and more of one ingredient or the other is added as experience dictates.

The first of these operations of the precipitation process—smelting the crude with iron—is called "singling," the second operation—resmelting the singles for the production of the bowl metal—is called "doubling," and the last operation is called "refining," or "frenching."

Direct Extraction of Metal from Ore or Crude.—(Reverberatory Bath Furnaces). Several patents have been taken out (Sanderson, Cookson, Herrenschmidt) on the direct smelting of antimony sulphide in a bath of ferrous sulphide, on the hearth of a reverberatory furnace. This method has given good results but has had no wide adoption commercially. After the hot ore has been charged into the reverberatory and thoroughly rabbled, iron is added together with a certain amount of soda ash, the temperature raised, and, when decomposition of stibnite by iron is complete, the antimony metal is tapped. The taphole is closed as soon as the iron sulphide appears. Slag is drawn through the working doors, and as the iron sulphide increases during the operation it is removed until the bath is reduced to its original depth.

At a smelter in Mayenne, France,[2] using a reverberatory furnace with a bed 10 ft. long by 4 ft. wide, the charge made up every 3 hr. was as follows:

[1] In Japan at the Saijo Smeltery, the Star Bowl metal carried 97 to 98 per cent Sb, 1.5 per cent Fe, and 0.7 to 0.8 per cent S.

[2] GOWLAND, "The Metallurgy of Non-ferrous Metals," revised by C. D. Bannister, 4th ed., 1936, pp. 570–575.

	Pounds
Rich ore (50 to 60 per cent Sb)	992
Worked ore fines (about 45 per cent Sb)	330
Slag from second or refining fusion (about 20 per cent Sb)	44
Sodium carbonate	44
Scrap iron	529

At the Wilhelmsberg Works, in Germany, reverberatory furnaces fired with gas were adopted for the smelting of the crude. The first smelting was done in a furnace having an elliptical hearth whose area was 300 × 500 cm. The charge was made up of 3000 kg. of crude and 1000 to 2000 kg. of iron, soda, salt, slag, and charcoal or anthracite. The use of powdered charcoal or anthracite was to prevent the excessive loss of antimony due to volatilization. The time required for the smelting was 5 to 6 hr., and the consumption of coal was 525 kg. per ton of the crude charged. The crude metal contained on an average 3.5 per cent Fe. The average result was Sb in the raw metal, 86 to 88 per cent; Sb in the slag, 8 to 10 per cent; loss due to volatilization, 4 to 6 per cent. This metal was refined in another reverberatory furnace, having a hearth area of 150 × 250 cm. The charge was made up of 1500 kg. of raw metal, plus soda, charcoal or anthracite, old refinery slag or couverture slag. Time required was ½ to ¾ hr., and the coal required was 400 kg. per ton of regulus produced. Average loss was 6.5 per cent, counting the antimony content of metal in the raw metal as well as that of the slag and couverture charged.

Water-jacket Blast-furnace Smelting.—The blast-furnace smelting of antimony ores, both sulphide and oxide, is entirely feasible and will undoubtedly come into more common use as the industry advances. Already, in Mexico, California, and England, successful blast-furnace smelting has been under way for several years, proceeding along lines only slightly modified from regular lead-smelting practice.

The operators of these blast-furnace plants are most enthusiastic regarding the advantages and ultimate general adoption of this method, asserting confidently that the first page of antimony metallurgy has hardly been written and that the blast-furnace process will extensively replace the old existing methods in the industry. That this may come about in Europe, Mexico, and America there is little question. Under existing ownerships and conditions in China, however, it is extremely improbable that any reshaping of the industry will take place.

Attempts to smelt unroasted stibnite ores in water-jacketed blast furnaces did not come to any successful result until recent years, and published information on the subject is exceedingly meager. There is a marked difference in the behavior of stibnite and that of other metallic sulphides in the blast furnace. It has been found best to add no metallic iron to the charge and to regulate the coke so as to preclude any reduction of ferrous oxide in the flux. No iron available for matte is provided, and matte is usually absent. Any addition, or presence, of metallic iron will always result in the production of an antimony-iron alloy—speiss.

It is usually found that the contents of the furnace crucible gradually freeze from the bottom upward, and the entire crucible is eventually a solid mass. It is frequently the practice to fill the crucible with firebrick and separate the mixed flow of slag and metal in a shallow reverberatory forehearth.

While the blast-furnace smelting of stibnite has not enjoyed the long industrial history of the volatilization and English precipitation methods, it is to be stated that the best conditions for the process appear to be less than 10 per cent of coke, low blast pressure, low metal content of the charge (about 10 per cent), high smelting column (over 15 ft.), and separation of slag and metal in a heated forehearth. In an efficient plant, the great bulk of the volatilized material is recovered in baghouses, but it is, of

ccurse, undesirable to have to re-treat a large amount of fine material unsuitable for blast-furnace work. The flue dust is best treated in a reverberatory, while the fume is useful in refining, or it may be used as raw material for the manufacture of antimony compounds.

The blast-furnace process does not appear to be adapted for the treatment of high-grade stibnite ore. Loss by volatilization is common to all forms of antimony smelting, and in this respect the blast furnace is far worse than the reverberatory, where a layer of flux or slag protects the metal. With low-grade material, however, which it is difficult or wasteful to treat by other methods, the blast furnace offers decided advantages, *i.e.*, where large quantities of poor ores, foul slags, mattes, or liquation residues have to be worked up. It is a favored mode of smelting for all materials containing about 25 to 40 per cent antimony, which can be mixed with fluxes to give a charge sufficiently poor in metal to hold down volatilization.

It is pointed out by Schoeller[1] that the production of antimony from stibnite in the blast furnace is an oxidizing process in which the metal is formed in two stages that proceed simultaneously; (1) the molten stibnite absorbs oxygen from the blast; (2) the oxide at once reacts with the unaltered sulphide (roast-reaction process) to form metal and sulphur dioxide, thus:

$$2Sb_2S_3 + 9O_2 = 2Sb_2O_3 + 6SO_2$$
$$2Sb_2O_3 + Sb_2S_3 = 6Sb + 3SO_2$$

In endorsing this theory of the blast-furnace process, it is realized that it has been a commonly held belief that antimony sulphide and trioxide do not react on each other as do the corresponding lead and copper compounds, but that the antimony compounds fuse together to an antimony glass. The latter reaction occurs, without question, if the oxide-sulphide mixture is fused in a crucible under a layer of salt, but if stibnite is roasted with insufficient access of air, some oxide will be formed which will react with the unaltered sulphide, part of the antimony settling out in a metallic state. The roast-reaction process does, therefore, have a part in the smelting of antimony. It appears, in some degree as well, in the process of liquation, the metallurgical operation carried on on a large scale in China, for the concentration by fire of antimony-sulphide ores. Examination of this crude discloses the fact that it is not pure antimony sulphide, but a complex solid solution, containing oxide and free metal. The molten sulphide in trickling down from the upper pot absorbs oxygen from the air rising from the crude already collected, which partly converts it to trioxide. This reacts with more sulphide to form metal and SO_2, which latter is carried away by the draft, allowing the reaction to proceed. Once the material has collected in the lower pot, the reaction is arrested on account of the lower temperature and the small surface exposed. It is thus proved that molten antimony sulphide by itself, in an air current, is partly converted into antimony, and the product also contains the trioxide.

The Mace Blast Furnace.[2]—The Mace blast furnace is a distinct improvement on the usual type of blast furnace for antimony smelting. The main variations from the old type blast furnace are (1) diametrically opposed rectangular tuyères below the shaft of the furnace in place of the circular tuyères spaced at regular intervals in the lower part of the water jackets, and (2) a removable crucible in place of a solid crucible built on the ground. There are several advantages in the use of the rectangular tuyères which extend the full length of the furnace on both sides. The

[1] Blast-furnace Smelting of Stibnite with Consideration on the Metallurgy of Antimony, *Trans. Inst. Mining Met.* (*London*), Vol. 27, pp. 237–267, 1917–1918.

[2] Private communication from H. C. Mace.

whole hearth area is active, and the dead spaces that exist between the tuyères of the older type furnaces are eliminated. This gives a uniform and intense combustion over the entire hearth.

On account of the open tuyère, the Mace furnace uses lower blast pressure (as low as 4 oz. per sq. in.) which is an important feature in continuous operation of the smaller units. The tuyères are so constructed that the opening into the furnace hearth can be adjusted. For oxidization and volatilization smelting, the slot is left wide open so that a large volume of air under low pressure can be admitted. For reduction smelting, the slot is narrowed. Another advantage of the open tuyère is that any accretions can be removed from the furnace by drawing them into the wind box with the hook instead of punching the dead material back into the furnace as is necessary with the circular tuyères. The advantages of the removable crucible are evident.

The antimony plant set up recently near Mexico City, Mexico, has a Mace furnace in operation. The ore treated is an oxide ore, containing a small amount of stibnite, having the following composition: Sb, 36.0; SiO_2, 48.0; S, 5.0; Fe, 1.05; Al_2O_3, 0.6; CaO, 2.0; MgO, 1.4 per cent.

The gangue is principally silica, running from 45 to 52 per cent, and the antimony runs from 35 to 38 per cent. Limestone and hematite are used for flux in the blast furnace to slag the silica, and the furnace charge is about 50 per cent ore and 50 per cent flux with 15 per cent of the weight of the charge coke. The furnace is run with a low column and a hot top to volatilize the maximum amount of the antimony. A small amount of antimony single metal, assaying 91 per cent antimony and 9 per cent iron, is produced, but no matte. The baghouse oxide assays 81.6 per cent antimony, and apparently the only impurity in it is a small amount of carbon dust from the coke. The baghouse oxide is mixed with 15 per cent fine charcoal and 6 per cent soda ash and is reduced in a reverberatory furnace to metal. The capacity of the furnace is 30 tons of charge in 24 hr.

Blast-furnace Smelting for Antimonial Lead.—The International Lead Refining Co.[1] treated antimony sulphide ore (25 to 60 per cent Sb, 6 to 45 per cent SiO_2) and antimony oxide ore (20 to 40 per cent Sb, 10 to 45 per cent SiO_2) in a blast furnace, in which were added the secondary materials, such as battery plates, battery mud, lead oxide, paint and other refinery skins, to furnish the lead required for marketable antimonial lead. The blast-furnace equipment consisted of two five-tuyère 42-in. round furnaces, connected by a flue to the baghouse. On account of the high zinc and arsenic content in lead refinery by-products, a slag of the composition SiO_2, 26 per cent; FeO, 40 per cent; CaO and ZnO, 20 to 24 per cent, was maintained. An average analysis of slag for 6 months showed that it contained Sb, 0.6 per cent and Pb, 2.36 per cent. The actual blast-furnace loss amounted to 2.4 per cent Sb and 1.50 per cent Pb. The furnace charge varied from 2500 to 3000 lb. with 13 per cent coke. Blast pressure was maintained at 10 to 12 oz. The two furnaces smelted 60 to 90 tons of lead and antimonial material per day, producing 30 to 35 tons of antimonial lead of the following composition: Sb, 13 per cent; Cu, 0.15 per cent; As 0.75, per cent; Pb, 86.1 per cent.

Antimonial Lead.—One example of production in the United States is at the Pittsburgh Plant of Federated Metals Co., where a circular blast furnace 42 in. diameter at the tuyères, with 10-ft. water jackets, treats approximately 100 tons per day of smelting stock made up of antimony-bearing lead battery plates and lugs (carrying 69 to 92 per cent Pb and about 4 per cent Sb), antimony ore, returned slag, limerock, 8.0 per cent coke, and 4 to 5 per cent scrap iron. Blast pressure is 24 oz. The antimony ore used has about 40 per cent Sb, 1 per cent Pb, and the antimony recovery is about 85 per cent of the total antimony smelted. The products are approximately

[1] HULST, Treating Antimony Ores, *Chem. & Met. Eng.*, Vol. 21, p. 727, 1919.

71 per cent antimonial lead metal (carrying 88.4 per cent Pb, 11.3 per cent Sb), 17 per cent discard slag, 2.3 per cent matte, and 10 per cent fume and dust.

Converters.—Sulphide ore of antimony can be smelted in a converter into which air is blown, but this is not a method in practical use. The air burns part of the sulphur of the ore, with the production of sulphurous acid and the metal itself. Antimony sulphide fumes are formed also, and these, if acted upon by a current of air, give antimony oxide.

The Hodson-Wang Process of Antimony Smelting.—An interesting combination of accepted methods of ore reduction is found in the Hodson-Wang continuous "flash" process,[1] which process utilizes the heat of the reduction reaction and also permits

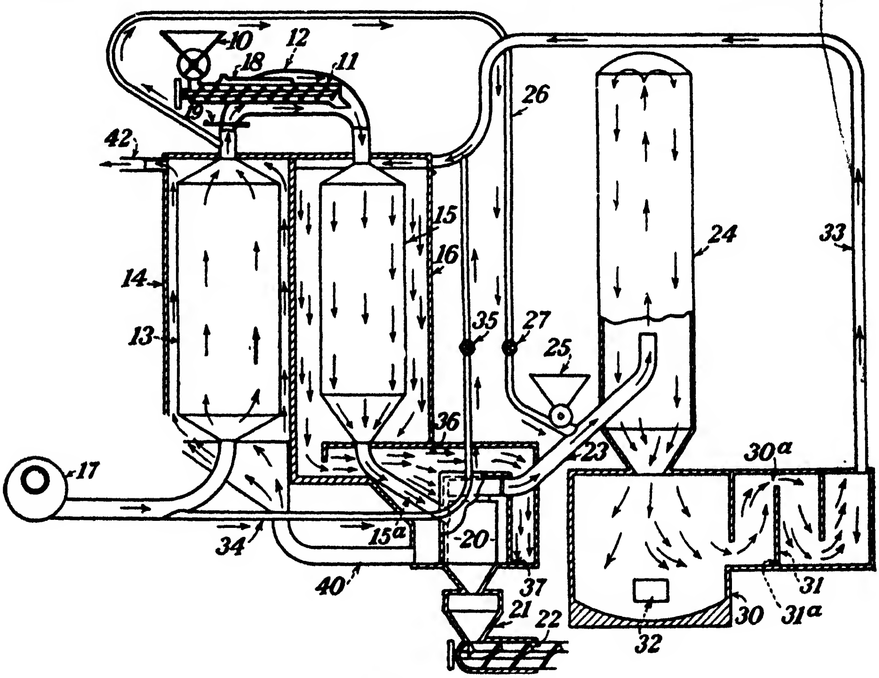


FIG. 18.—Hodson-Wang antimony process.

removal of all gangue from the ore during roasting treatment. Pulverized ore is generally used, although one adaptation of the process is designed for use of lump ore. The crude ore is roasted in an externally heated vertical or horizontal chamber by waste gases from the reduction furnace. Antimony in the ore is carried off to the main reduction chamber as trioxide gas, and all gangue matter drops to the bottom of the first chamber. The volatile trioxide formed is injected directly into a vertical shaft furnace with gaseous media (or with preheated air and carbon), and the mixture of reducing gas and oxide particles is kept in violently turbulent motion by a sudden reversal of direction. This agitation in the reducing gas promotes speed of reaction and prevents formation of an envelope of nonreducing gas around the oxide particles. The reduced metal, in fine liquid form, is collected in a lower chamber. With arsenical ores, usually sulphide, the arsenic forms volatile arsenic trioxide in the first, roasting, chamber together with the antimony trioxide. It will be reduced along with anti-

[1] (U.S. patent 2295039, Sept. 8, 1942.) Granted in the United States, Canada, Mexico, and Bolivia; applied for in Italy, Japan, Germany, Brazil, Belgium.

mony in the second chamber. However, as arsenic sublimes at a temperature of 615°C. and the reduction furnace is kept at about 800°, the antimony condenses out as a liquid, while arsenic remains a vapor and can be carried off with the gases for subsequent collection.

By-products of Antimony Smelting.—The by-products produced in the foregoing processes include liquation residues, matte, slags, and flue dust. The slags obtained from the extraction by the roasting and reduction method consist principally of silicates; those from the precipitation method, silicates and sulphides. They are thrown away if not sufficiently rich to be used in the first smelting of the ores. The other by-products are all added to the charges in smelting the ores, the liquation dross being first roasted. The flue dust is intimately mixed with soda ash, before smelting. Liquation residues are also sometimes treated separately in shaft furnaces.

The extraction by wet methods of antimony from its ores has had much attention in European centers, but it is still a matter of academic discussion, rather than practical application. Solution of stibnite is readily effected in sodium sulphide, sodium hydroxide, or calcium sulphide, and from such solutions antimony sulphide is precipitated by carbon dioxide or sulphurous acid. There is little evidence, however, that commercial recovery of antimony from its ores by wet methods has come about.

It is recognized that in the treatment of ores containing a mixture of the sulphides of antimony and lead, it would be difficult to separate the two metals. The study of Wagenmann[1] establishes the fact that in order to separate the lead sulphide from such a mixture by a solution of Na_2S, the two sulphides present in the mixture must satisfy the chemical formula $2PbS.Sb_2S_3$ or $Pb_2Sb_2S_5$ so that the reaction $Pb_2Sb_2S_5 + 2Na_2S = Na_4Sb_2S_5 + 2PbS$ would take place. In other words, when the Sb_2S_3 in the mixture is less than 41 per cent, enough Sb_2S_3 must be melted with the mixture in order to bring it up to 41 per cent.

Electrolytic Extraction of Antimony.—The supply of antimony for the world's needs to date has come almost entirely through the application of dry methods. Poor antimony ores either have not been used in the past, or have been subjected to a volatilizing roast, with subsequent reduction of the trioxide, usually in reverberatory furnaces. This is, however, a somewhat laborious metallurgical operation, and the application of electrolytic methods as a means of extraction from poor ores has long been desired.

During the high-price years, a small electrolytic production occurred, the solvent being a 6 per cent sodium hydroxide solution, which gives an extraction without serious contamination with other metals.

This solution, electrolyzed, deposits antimony of a very high purity, but in ordinary times the deposition of the antimony and the necessary regeneration of the electrolyte are too costly to make the process commercial. The chief difficulty is a troublesome accumulation of thiosulphate at the anode, which blocks the commercial success of the electrolytic process.

When the solution is electrolyzed, the reaction at the cathode seems to be

$$Na_3SbS_3 + 3H = Sb + 3NaSH$$

while at the anode, sodium thiosulphate and Na_2S_2 are formed by oxidation. The 6 per cent NaOH solution holds about 3 per cent antimony at first, but as thiosulphate accumulates, the solvent power decreases until there has accumulated one atom of sulphur for each atom of sodium present, when the solvent power has dropped to about 0.7 per cent. When this amount of sulphur has gone into solution, the iron anode commences to be attacked and falls to pieces rapidly. A practical insoluble

[1] Borchers, Zinn, Wismut, Antimon, "Metallhuttenbetriebe," Vol. 4 pp. 134–136, W. Knapp, Halle, 1924.

anode has not been found. The continuance of the process beyond the point at which the sulphur in solution commences to be in a larger atomic percentage than the sodium requires the regeneration of the solution, or furnishing a new one. If a new solution is applied, it means the consumption of 1 lb. of NaOH per pound of antimony.

The best way to handle this situation seems to be the proposal by Demorest to evaporate the solution to dryness with exhaust steam; roast the residue in a reverberatory furnace to get rid of about half the sulphur, thus changing the thiosulphate to sulphate; then mix with coal and heat until it has all been reduced to Na_2S, which quickly dissolves stibnite and can be put into the circuit again. Small-scale experiment shows this to be successful, but it has not been tried on a large scale.

J. Koster and M. B. Royer[1] have developed a novel electrolytic process for the treatment of antimonial gold concentrates from ores found in the Yellow Pine Mine at Stibnite, Idaho, of the following composition: Au, 1.66 oz. per ton; Ag, 6.34 oz. per ton; Sb, 15.6 per cent; As, 5.5 per cent; Fe, 19.1 per cent; S, 25.0 per cent. This concentrate was first smelted with iron and soda ash in the proportion of 4:1:1; the crude metal obtained, to be cast into anodes, had this composition: Au, 8.4 oz. per ton; Ag, 14.6 oz. per ton; Sb, 60.7 per cent; As, 7.5 per cent; Fe, 27.4 per cent; S, 5.9 per cent.

"The electrolyte was prepared either by solution of antimony metal in sulphuric acid, evaporating to fumes of SO_3, and solution of the white pasty mass in concentrated hydrofluoric acid; or solution of antimony oxide in concentrated hydrofluoric acid, filtering undissolved matter, adding concentrated acid, and diluting to 80 g. Sb and 500 g. sulphuric acid per liter."

The crude metal from the smelting operation was cast into anodes in vertical molds $4 \times 7 \times 3/4$ in. The cathodes were of 16-gauge sheet copper and were 1/4 in. longer and 1/2 in. wider than the anode. The most satisfactory current density was found at 6 amp. per sq. ft. Current efficiency was found to be 99 to 100 per cent.

The cathode metal was found to have the following analysis: Au, trace; Ag, 1.1 to 1.5 oz. per ton; Sb, 91 to 96 per cent; As, 3 to 7 per cent; Fe, 0.2 to 0.4 per cent; S, 0.06 to 0.09 per cent. This cathode metal, after purification by fusion with slag consisting of equal parts of NaOH, NaCl, Na_2CO_3, and $NaNO_3$, followed by a starring fusion with 3 parts K_2CO_3 and 2 parts Sb_2S_3, was found to have an analysis of Sb, 99.73 per cent; As, 0.19 per cent; Fe, 0.06 per cent; S, 0.02 per cent. The anode slime, containing most of the precious metals, was found to have an analysis of Au, 70 to 133 oz. per ton (80 to 94 per cent recovery); Ag, 114 to 237 oz. per ton (30 to 48 per cent recovery); Sb, 4 to 8 per cent; As, 6 to 24 per cent; Fe, 35 to 45 per cent; S, 14 to 28 per cent. The matte from the precious smelting contained, upon analysis: Au, 0.26 oz. per ton (7 per cent recovery); Ag, 5.9 oz. per ton (50 per cent recovery); Sb, 3.1 per cent (11 per cent recovery); As, 0.8 per cent; Fe, 52.6 per cent; S, 32.1 per cent. The recovery of antimony was found to be 80 to 90 per cent, from concentrate to marketable metal.

Electrolytic Antimony.[2]—At the Bunker Hill and Sullivan Mining & Concentrating Co., Idaho, tetrahedrite, $3Cu_2S.Sb_2S_3$, concentrates mixed with Na_2CO_3, Na_2SO_4, and coal are fed to a three-electrode electric furnace. Current, at 50 to 110 volts, flowing from electrode to furnace wall, the charge serving as the resistance, yields a melt temperature of about 2300°F. Matte is tapped from the furnace, cooled, and crushed to pass 80 mesh. The ground matte is leached with sodium sulphide solution at 140°F. to form the electrolyte. Undissolved pulp is crushed and tabled to yield a concentrate of Sb-Bi-Ag alloy and a tailing containing 25 to 30 per cent Cu and 1 per cent Sb, the latter being added to the copper-smelter charge. From the electrolyte

[1] Electrolytic Recovery of Antimony from Antimonial Gold Ores, *U. S. Bur. Mines Rept. Investigation* 3491, February, 1940.

[2] *Mining World*, Vol. 4, No. 6, pp. 3–9, 1942.

containing the thioantimonate, Na_3SbS_4, antimony is deposited on sheet steel cathodes, the anodes being sheet lead. The anodes are in a compartment formed of heavy sail cloth as a diaphragm. There is no material corrosion of either electrode at operating current density of 20 amp. per sq. ft. Cathodes are stripped of their antimony each 6 days. Spent electrolyte containing about 2 to 5 g. per l. is recycled back to the leaching tanks after a treatment with sufficient barium sulphide to precipitate the sulphate ions present. The precipitated barium sulphate is reduced to sulphide for re-use as a precipitant. The antimony, being brittle, is easily removed from the cathodes. This plant, erected at a cost of about $500,000, started operations in March, 1940.

Refining of Antimony Metal.—Unrefined antimony usually contains sulphur, iron, arsenic and copper, and lead. These impurities, with the exception of lead, can be eliminated partly by oxidizing and slagging agents, partly by sulphurizing agents, and partly by chlorinating agents. Soda, potash, or antimony glass (antimony oxysulphide) removes sulphur by fusion and converts arsenic into arsenate of soda or potash. The conversion of copper and iron into their sulphides by sulphide of antimony can be facilitated by the addition of soda or potash, or of Glauber's salt and charcoal. These sulphides form a slag with the sulphide of sodium produced from the reduction of the Glauber's salt, with the soda or potash present. These sulphides are easily removed by antimony glass.

The use of common salt, carnallite, or magnesium chloride to volatilize some of the foreign metals present as chlorides, and to slag others, may occasion great loss of metal due to volatilization. It is somewhat difficult to remove the lead, and when antimony ores are found to contain a considerable percentage of lead, as is frequently the case, they may with advantage be smelted with lead ores to produce hard, or antimonial, lead (12 to 15 per cent Sb).

One of the most objectionable impurities found in antimony is arsenic, because great loss of the metal and expense are entailed when one tries to bring the arsenic down to the market tolerance. Obviously, the best way to obviate this difficulty is to free it as much as possible from the ore before it is smelted. This can be done by differential flotation of the arsenic mineral, as will be described later, or as suggested by Koster and Royer,[1] by roasting the ground ore or concentrate at 475 to 500°C. with steam at atmospheric pressure, when approximately 88 per cent of the original arsenic will volatilize off with only a loss of about 10 to 15 per cent antimony.

If the antimony oxide, obtained in the volatilization process, contains arsenious oxide, say as high as 2 to 3 per cent, the following method can be adopted for its partial elimination.

1. Heat the oxide in a muffle furnace to above 200°C. whereby the As_2O_3 is volatilized while the Sb_2O_3 may remain as Sb_2O_3 or partially change to Sb_2O_4. Constant rabbling is necessary. In an experiment by C. C. Chao in the laboratory of the National Bureau of Mining and Metallurgical Research, China, the arsenious oxide was brought down from 2.38 to 1.55 per cent at a temperature of about 300°C.

2. The arsenious oxide can be brought down from 2.38 to 0.54 per cent by digesting the antimony oxide with hot water and $0.5N$ HCl for 4 to 5 hr.

To reduce the amount of arsenic contained in the regulus, the following method can be adopted. After covering the molten metal with soda ash, air is blown into it. In three successive operations, occupying about 2 hr., the arsenic content can be brought down from 1 to 0.1 per cent. The soda ash used is about 2½ per cent by weight of the bath in each operation. The soda ash in the slag produced can be regenerated by a simple process.

[1] *U. S. Bur. Mines Rept. Investigation* 3491.

A similar method of refining antimony by blowing air through the molten metal has been worked out by G. A. Merson, L. Ya Krol, and O. E. Krein.[1] According to them, the following optimum conditions are recommended for carrying out the refining treatment, which reduces the arsenic content in the metal from 0.70 to 0.05 per cent.

1. Temperature—950°C.
2. Air supply for blowing—500 ml. per min. per kg. of metal.
3. Amount of soda slag—20 per cent; the slag is renewed once during refining.
4. Duration of refining—1 hr. under each slag, *i.e.*, a total time of 2 hr.

Under the above conditions a yield of 89.5 per cent refined antimony was obtained. Of the remaining 10.5 per cent, 8.75 per cent passed into the slag, while 1.75 per cent volatilized off as Sb_2O_3.

Another method to refine antimony containing an appreciable amount of arsenic is to melt the metal, which is crushed to 10 to 15 mesh with, say, 5 per cent niter and about the same amount of soda ash.

Starring.—It has long been the practice of the trade to judge the purity of refined antimony by the development of a fernlike structure, or "stars," on the surface of the ingot. The appearance of this structure does not actually indicate the relative purity of the metal, but is only the result of cooling it slowly under cover of a layer of a properly prepared starring mixture—couverture—a slag that has a fusion point lower than that of antimony, which is 630°C. When the regulus contains impurities like sulphur, arsenic, lead, or iron, to any appreciable extent, its surface shows the presence of these foreign elements by specks, by a leaden appearance, or by a poorly defined appearance of the fernlike structure. It is true, on the other hand, that regulus containing impurities above what are considered to be the limits imposed by the market often shows stars as bright and well defined as those of well-refined regulus. Since buyers demand this artificial adornment on the regulus, the starring operation has become a regular part of the refining process, adding an unnecessary cost of $5 to $30 per ton.

Different mixtures for this couverture are shown in Table 2 by the authors, as used, according to local conditions, by various antimony smelters in China.

Another starring mixture for pure Chinese ores, patented by C. Y. Wang in 1918 with the object of avoiding the use of mixtures containing any antimony compound, utilizes iron sulphide, which is generally discarded from the precipitation process of antimony smelting as useless. This by-product takes the place of antimony compound and is used with any suitable alkali compound, preferably potassium carbonate. The proportions of the mixture are as follows: iron sulphide, 9 to 14 parts; potassium carbonate, 8 parts.

In England the process of refining and restarring the star bowls, also a pot-furnace operation, is as follows: The lumps of metal, when cold, are removed from the mold and are thoroughly cleaned from the adhering skin of slag by chipping with sharp hammers, this part of the work being sometimes done by women. Unless this cleaning process is carefully done, it is well-nigh impossible to obtain good stars on the finished metal. The chippings are returned to the second smelting. Having been cleaned, the star bowls are broken small. The charge made is about 84 lb., together with enough flux to surround the ingots completely; the quantity is generally 8 lb. for ingots of the ordinary shape. The melting takes place in the crucibles standing close to the fireplaces, where the fusion is most rapid. The metal is charged first and is closely watched; as soon as it begins to melt, the flux is added; and as soon as the fusion appears to be complete, the furnaceman stirs the mixture once round only, with an iron rod, and the charge is then poured out. The flux is used over and over again,

[1] *Jour. Applied Chem.* (*U.S.S.R.*), Vol. 13, pp. 323–328, 1940; abstracted in the *Metal Ind.* (*London*), June 13, 1941, pp. 505–506.

being regenerated by the addition of carbonate of potash. The ingots must be completely surrounded by the flux; there must be a thin layer of it between the mold and the metal, and also the whole surface of the ingot must be covered by the flux to a depth of ¼ in. Any traces of the flux still adhering to the ingot are removed by washing in warm water, with the assistance of a little sharp sand.

TABLE 2.—COUVERTURE MIXTURES

Couverture	Crude (high-grade), Sb_2S_3	Antimony tetroxide (well-roasted crude), Sb_2O_4	Antimony trioxide, Sb_2O_3	Potash, K_2CO_3	Soda ash, Na_2CO_3	Charcoal, C	Smelters using the mixtures
I	15	24	...	10	1	1.25	Pao Tai
II	15	24	...	11	3	1.25	Pao Tai
III	2.2	13.2	...	7.5	....	5.7	To-cheng
IV	4.5	....	20	.....	5	0.5	Loong Kee
V	7	....	18	.....	4	0.5	Tai Wo
VI	3–4	....	32	.....	2–4	1	
VII	5	30	...	.....	5–6	1	Pao Tai
VIII	....	....	85	.....	15	....	Wah Chang
IX	....	....	4–5	1–2.5	...	....	Wah Chang
X	....	....	8	1			
XI	....	....	40	1	4		
XII	....	....	7	.....	1	....	Loong Kee
XIII	6	....	16[a]	.....	1	0.5	Pao Tai
XIV	7	14	...	.....	0.5	0.5	Pao Tai

[a] Pure flue dust.

For a charge of 60 to 70 lb. of bowl metal, with 1 to 2 lb. of potash and 10 lb. of slag, obtained from a previous charge of French metal, the time required is ¾ hr.

Refining in Reverberatory Furnaces.—The refining operation is in most cases carried on in a small furnace, of reverberatory type, and proceeds about as follows: 1200 to 1500 lb. of impure antimony is melted as one charge, to which is added 3 to 7 per cent of soda, mixed with a little coke dust or fine charcoal. The slag from this fusion gradually becomes thicker and thicker, and after about 3 hr. is skimmed off through the working door. Up to this point, the iron and sulphur remain as impurities in the metal. They are next removed by adding ingredients capable of forming antimony glass, such as oxysulphide of antimony. For each 100 lb. of antimony in the charge, 3 lb. of liquated sulphide of antimony and 1½ lb. of antimony tetroxide are thrown in, and as soon as these are fused, 4½ lb. of potash is added. Care is taken that the bath of metal is completely covered with the fluxes.

The metal can be ladled out, after another 15 min., being handled cautiously, in order to secure the starred appearance of the ingots. Three charges of about 1500 lb. each can be refined in one of the small furnaces used, in 24 hr., with a coal consumption of 1300 lb.

The slag obtained in the final step of the refining operation is called "star slag" and consists principally of antimony glass, carrying 20 to 60 per cent antimony. It is used repeatedly for refining, until it becomes too impure for the purpose, when it is

charged along with the ore for the first smelting. The other slags obtained in the course of refining are also added to the ore-smelting charges.

The proper procedure for charging any of the above mixtures is as follows: The compound, after being thoroughly mixed, is immediately charged into the reduction furnace as soon as the skimming is finished. The doors are closed, and vigorous firing is maintained; as soon as it is observed that the mixture is completely melted, ladling commences. Each ladle dips into the molten metal and, in coming out, picks up a certain quantity of the molten couverture, which, when poured out together with the metal into a hold mold, completely covers the metal on all sides. Ladling must be done rapidly for each moldful—four or five ladles to one slab of regulus according to the size of the ladle used. The thickness of the solidified couverture varies from 1 to 2 mm. on all sides except the top, which varies from 5 to 7 mm. The amount of couverture required for each charge varies from one-sixth to one-fourth the weight of the regulus produced. It is remarkable that generally the weight of the solidified couverture hammered off from the slab after cooling is less than the original weight of the mixture put in by about one-third, owing in part to volatilization and in part to wall-fluxing during melting. The couverture can be used over again the second or third time, sometimes with an addition of a little soda, until it is so contaminated with impurities that it cannot produce any good stars. Then the worn-out couverture is mixed with the ordinary charge of trioxide or tetroxide and calculated as an equivalent amount of soda required for that charge. In connection with this, the practice at the Loong Kee and the Pao Tai smelters may be mentioned: The Loong Kee smelter uses, for every 14 tons of regulus produced, 1.14 tons of couverture which, according to couverture XII of Table 2, contains 1 ton of trioxide and 0.14 tons of soda. The Pao Tai smelter uses 1 ton of couverture XIV for 14.5 tons of regulus.

TABLE 3

Name of brands	Sb	Cu	Fe	Pb		Sn	Zn	S	Others
W. C. C. (Chinese)	99.848	Trace	0.009	Trace	0.095	0.030	Trace	0.018	Cd, trace
Hallett's	99.856	0.046	0 007	0.718	0.210	0.012	0.023	0.128	
Cookson's	99.	.046	0 004	0.102	0.092	Trace	0.034	0.086	Co, Ni 0.028
Japanese	99.195	0.043	0 007	0.424	0.095	0.012	0.023	0.201	
Chinese	99.760	0.012	0 004	0.029	0 090		0.027	0.078	Co, Ni, trace
La Lucette	99.35	0.010	0 060	0.130	0.200		...	0.200	
U. S. "Lone Star"	99.70				050	(No other single impurity in			
U. S. "R.M.M."	99.30				10	excess of 0.10 per cent)			
Czechoslovakia	99.70	Trace	0.110	0.04	070		...	0.050	
	99.70	Trace	0.056	Trace	0 031			0.119	Ni, Sn, trace
Yugoslavia	99.34		0.11	0.04	30			0.080	

NOTE: English antimony generally commands a premium over foreign brands, especially the "C" Brand of Cookson's, which is recognized as the world's standard antimony.

A procedure, as adopted by W. Brazenall[1] for starring the regulus produced, is as follows: "The flux furnace was 4 × 3 ft. It was heated by wood fuel, and kept at a low temperature. It was tapped into a large pot and ladled out by small ladles into the metal ladles just before pouring. The metal ladles were placed under the taphole of the metal furnace, one on the floor and the other on bars above it, close to the spout of the furnace. Then the bar was drawn, allowing the metal to flow into the ladles, into which enough flux had been poured to cover two bars. The molds,

[1] *Chem. Eng. Mining Rev.*, June 6, 1932.

10 × 10 × 3 in., were placed in rows adjoining each other, and a gate of iron was placed above them with a hole at each end reaching to the center of the molds, so that both molds were poured simultaneously. The flux floating on top of the molten metal flowed into the mold with the metal, thus completely covering it. This is essential for starring the metal, as it excludes the air from it. This method of pouring the metal was devised by the writer Brazenall at the works of the Western Metal Co., Harbour City, Calif., after a great deal of experimentation, in order to avoid ladling from the furnace with iron ladles, as they soon wear out and burn away, the iron then going into the metal."

Typical analyses of refined antimony supplied by English, Chinese, American, French, Czechoslovakian and Yugoslav producers are shown in Table 3.

Ore Dressing.—Beneficiation of low-grade sulphide ores of antimony by means of ore dressing has been tried both experimentally and in practice and has given indication that in the future it will form a beneficial adjunct to metallurgical treatment.

It is undeniable that it is better to free the arsenic, if present in the antimony ore in an appreciable quantity, at the very beginning by differential flotation before smelting than, to resort to the laborious and expensive methods of treating the final metal for its elimination.

There occur, in many parts of the world, scattered deposits of low-grade ores of antimony for which the building of a metallurgical plant is unwarranted. For their exploitation, beneficiation of the ores is highly desirable in order that the concentrates be profitably shipped to other centers for metallurgical treatment. Sometimes, associated with the antimony ores are gold and silver, which, in the same dressing operation, are at the same time concentrated. But the general problem of concentrating low-grade oxide ores of antimony is still awaiting solution.

A few instances of past experiments and current practices are now given, to show the trend of the development of the dressing of antimonial ores.

The Flotation Plant at Djinli Kaya Mine in Turkey.[1]—The flow sheet is as follows: From ore bin to ball mill about one of water to two of ore by weight was used. The mill discharge passed to the Dorr classifier, and sufficient water was added here to make a pulp of 2½ or 3 of water to 1 of ore. The pulp passed to the larger steady head tank where more water was added when required to bring the dilution up to 4 of water to 1 of ore, and thence to the fourth cell of a 12-cell flotation machine. The reagents used were creosote, naphtha, cresylic acid, xanthate, cyanide, soda ash, lime. The use of reagents depended on the type of ore to be treated and the acidity or alkalinity of the water available. It was essential that the pulp be slightly alkaline. The ore consisted of 10 to 20 per cent Sb and 0.5 to 10 per cent pyrite in a relatively soft siliceous gangue. The mine water used had to be neutralized by the addition of soda ash or lime.

A concentrate carrying 60 to 65 per cent Sb and tailings of 1 to 2 per cent Sb was aimed at. Cyanide was used to depress the pyrite. The function of the creosote, oils naphtha, and cresylic acid was mainly to coat the small bubbles of the froth to which the shining particles of sulphide adhered. Xanthate was most useful in cleaning up the tailings. Very little, if any, of this reagent was used before the pulp had reached the seventh or eighth cell of the machine, the froth from these cells being returned to the machine and refloated. The order of the feed of the reagents was as follows: Mixture of creosote and cresylic acid in ratio of 1:2 at 4 lb. per ton to No. 4 cell; cyanide at 0.5 lb. per ton to No. 1 cell; lime or soda at 0.6 lb. per ton to overflow from classifier.

Differential Flotation Work at the Wiluna Gold Mine, Wiluna, Australia.[2]—A bulk concentrate containing arsenic and iron sulphide together with antimony is

[1] Lawrence, *Mining & Met. Soc. Bull.* Vol. 7, July, 1933–March, 1934.

[2] Private communication.

floated in a Fagergren machine. The antimony content of the feed to this machine varies from 0.2 to 2 per cent. The bulk concentrate contains 4 to 20 per cent, depending on the grade of the crude oil.

Xanthates and lead sulphate with pine oil and cresylic acid are the reagents used in this circuit. Alkalinity is controlled by the addition of soda ash. The bulk concentrate is then passed to a series of cleaning machines where the pyrite (and arsenopyrite) is depressed by the addition of caustic soda and cyanide and other reagents. The success of the operation depends on the accurate control of depressants in the first stage and, subsequently, the control of depressants in the cleaning circuit and the points where they are introduced. To produce a 60 per cent Sb concentrate, 6 to 10 cleaning operations are necessary.

Differential flotation of an arseniferous-sulphide ore of antimony, containing gold, has been practiced at the Cucuma mine, Czechoslovakia.[1] For the flotation of 1 ton of 6 per cent Sb ore to concentrates containing 60 per cent Sb, the following reagents were required: H_2SO_4, 8800 g.; xantol, 80 g.; ethyl xantogen, 115 g. To separate the associated arsenic, the reagents required were: Na_2S, 345 g.; Na_2CO_3, 580 g.; sapinol, 42 g.; butyl xantogen, 115 g.

The Yellow Pine Mine, Stibnite, Idaho,[2] uses flotation to concentrate the gold-silver-antimony ore. The heads averaged 1.85 per cent Sb, $4.75 in gold, and about ¼ oz. of silver per ton. The following reagents were used in the flotation of stibnite:

	Pounds per Ton
Copper sulphate	1.21
Soda ash	0.03
Caustic soda	1.37
Chlorine	0.82
Cresylic acid	0.30

Flotation resulted in a stibnite concentrate containing 0.77 oz. per ton of gold, $10.51 in silver, and 48.60% antimony.

Dry Concentration.—It is known that wet gravity concentrations of antimony ore with jigs and tables give rise to much slime loss. Experiment with dry concentration on dry concentrating tables, such as those manufactured by Sutton, Steele & Steele, Inc., Dallas, Tex., has shown that it is possible to concentrate a sulphide ore of antimony containing 8.56 per cent Sb to concentrates containing 65 to 70 per cent Sb and middlings containing 22 to 30 per cent Sb, which together represent 88 per cent recovery. The antimony content of the tailings amounts to 0.60 to 1.30 per cent Sb. The optimum size for this particular ore was found to be minus 28 to plus 35 mesh.

It is generally felt that antimony oxide ore does not respond to flotation. The Adelaide School of Mines, however, has recently found that it is possible to float cervantite at pH 7 after sulphidizing with sodium sulphide.

Résumé of Antimony Metallurgy.—The sulphide ore, stibnite, is the only ore of practical importance; the oxide ores, valentinite, senarmontite, or cervantite, being of minor significance. Beneficiation of low-grade ores by gravity concentration, air concentration, and flotation is under way or planned in all the producing regions where freight to distant smelting points must be considered or where the ore contains valuable constituents other than antimony. In the case of an ore containing an appreciable amount of arsenopyrite, it is sometimes advisable to use differential flotation to get rid of the arsenopyrite, which would otherwise contaminate the product resulting from the pyrometallurgical treatment of such ore. Of all the concentration methods, flotation appears to be by far the most satisfactory method and will undoubtedly find a place in antimony processing.

[1] Private communication.

[2] *U. S. Bur. Mines Information Circ.* 7194, January, 1942.

As a rule, concentration methods for antimony minerals have in the past shown unsatisfactory percentages of recovery due to dust losses. The relatively high frangibility of antimony ores results in heavy dusting, at crushers and screens, and the metal content of the dust is unusually high. For example, in dust from ore carrying 5 to 6 per cent metal, the metal content collected in dustproof housings and baghouse has been found concentrated to 15 to 20 per cent. The amount of dust collectible from antimony ore properly trapped may be as high as 10 per cent of the ore treated. In plants now under discussion, this type of dust will be concentrated by delivering it to the flotation cell along with the finer ore screenings. Dustproof housings installed with air concentrating tables are expected[1] to extend the use of dry concentration (air flotation) in many low-grade antimony districts.

As to hydrometallurgical or electrolytic methods of extracting antimony, they are uneconomical and only under exceptionally high prices and special circumstances may their adoption be recommended.

It is to be emphasized that, whatever smelting method is followed, an antimony plant must have a particularly good flue and condensing system. We know that with ordinary settling devices, such as flues with reduction or expansion of cross sections, Freudenberg plates or Roesing wires, only dusts larger than 10 microns (10^{-3} cm.) can be deposited; hence antimony fumes, whose particles range from 0.3 to 1.0 micron, and settle very slowly even in still air, cannot be effectively deposited. The usual cyclone dust catcher acts very ineffectively with antimony fumes; even the best cyclone, the so-called multiclone,[2] cannot settle particles smaller than 5 microns. Filtration of antimony fumes by means of bag filters, woolen or cotton, has been more or less adopted in many antimony works.

The Cottrell process of electrical precipitation has been adopted in a few antimony works and has proved its worth as a secondary cleaner for the oxide fumes.

The scrubbing or washing of antimony fumes, involving, as it does, the intimate mingling of the fumes by means of sprays or jets of water, is not thoroughly effective in precipitating the oxide. However, the Peabody process,[3] as recently developed in England, is a distinct improvement on the old-time scrubber and is a device that may be applicable to the condensation of antimony fumes.

For different grades of ore, the following methods are generally adopted:

1. For sulphide ore containing about 20 per cent Sb, the volatilization method.
2. For sulphide ore containing about 35 per cent Sb, the blast-furnace method.
3. For sulphide ore containing about 50 per cent Sb, the liquation method and the English precipitation method.
4. For oxide ore containing about 30 per cent Sb, the blast-furnace method.
5. For oxide ore containing about 50 per cent Sb, the direct reduction method.
6. For mixture of sulphide and oxide ore, the blast-furnace method.

It is to be noted that dead roasting of sulphide ore to the stable tetroxide, as a process for the treatment of rich ore, has become obsolete.

Production Economics.—The average yearly world production of antimony, including crude and oxide in Sb content, during the period from 1908 to 1938 was about 27,700 metric tons (China 62 per cent, Mexico and Bolivia, each about 11 per cent, totaling about 84 per cent of the world production, leaving about 16 per cent supplied by the United States, Algeria, France, Czechoslovakia, Italy, Yugoslavia, Peru and Argentina, with insignificant outputs from other countries).

[1] Allen H. Smith, patent pending.

[2] For an analysis of mechanical methods of dust collection see LISSMAN, *Chem. & Met. Eng.*, October, 1930, pp. 630–634.

[3] R. R. HARMON, Removal of Suspended Matter from Industrial Gases, *The Institute of Fuel*, London, April, 1938.

Increased demand, war born, for strategic metals has been coincident with global shifting in sources of raw material. In no commodity has the supply picture shifted more extensively than for antimony. In comparison to the normal movement of 65 to 70 per cent of world supply from China and 30 to 35 per cent from other sources in the 8 years prior to the Sino-Japanese War, the years of 1942 and 1943 draw approximately 49 per cent of world production of new metal from Mexico, 35 per cent from Bolivia and Peru, 14 per cent from the United States, and 2 per cent from various other regions. This is a forced draft on these last-named world areas, and it is believed probable that postwar economics will turn the searchlight back to the preponderant Chinese supply. Though actual Chinese export to the United Nations has dwindled to almost nothing, production in the Asiatic fields has continued in varying degrees as a matter of national economy and human livelihood, and Chinese stock piles of antimony—ore and metal, exact quantities unknown—are accumulating as a cushion for such postwar raw-material exhaustion as may develop.

Return of commodity normalcy, postwar, is expected to register, in the antimony industry: (1) 25 per cent shrinkage, by and large, of current world demand; (2) inability of Western Hemisphere areas, recently prolific, to maintain preponderance of supply; (3) reversion to Asiatic supply area.

Under normal conditions the relatively high cost of production in the United States from labor and deposit angles prevents successful competition with Chinese metal. The antimony-producing countries of the world may be divided into three groups:

1. Principal potential production, in order of importance: China, Mexico, Bolivia.
2. Irregular in normal times but with potential reserves available at higher price levels: The United States, Yugoslavia, Peru, Czechoslovakia, Algeria, Italy, Australia, French and Spanish Morocco, Canada, Turkey (Asia Minor).
3. Production small, known reserves probably less important: Hungary, Russia, Argentina, Portugal, Burma, Indo-China, British India, Japan, Southern Rhodesia, South Africa, Borneo, Greece.

CHAPTER VI

BISMUTH

BY WALTER C. SMITH[1]

History.—The metal bismuth has been known since the Middle Ages. Agricola refers to it as a form of lead and describes a method of separation from its associated minerals by liquation. The impure bismuth of the early writers was often confused with antimony, tin, and zinc. During the eighteenth century, bismuth was identified as a metallic element.

Occurrence and Properties.—Bismuth is rather widely distributed, but is not an abundant metal. It occurs as native metal, oxide, carbonate, sulphide, and as a constituent of many complex minerals. The supply of bismuth is derived from two principal sources: (1) bismuth ores mined and treated for their bismuth content; (2) ores mined and treated primarily for other metals in which bismuth is a minor constituent and from which it is recovered as a by-product.

Bismuth is a coarsely crystalline brittle metal, tin white in color, but with a distinct reddish tinge and a high luster. It has the atomic number 83 and an atomic weight of 209. Bismuth crystals are trigonal or rhombohedral. Bismuth crystallizes in a rhombohedral face-centered or deformed simple cubic lattice; the lattice constant $a = 4.726$ angstrom units. The unit rhomb contains 8 atoms.[2]

The density of bismuth is 9.80 g. per cc. at 20°C. and 10.067 at the melting point. The density of molten bismuth decreases regularly as the temperature rises, from 10.062 g. per cc. at 275°C. to 9.611 at 650°C. Expansion of the metal during solidification amounts to 3.32 per cent of its solid volume at the melting point. The compressibility is 2.8×10^{-6}, between 100 and 500 megabars, when the compressibility is defined as the average fractional change of volume caused by 1 megabar pressure. The hardness of commercial bismuth is 7.3 on the Brinell scale, using a 6.35-mm. ball and a 40.3-kg. load at 20°C., and 2+ on the Mohs scale.

The melting point of pure bismuth is 271°C. The mean specific heat for the metal up to the melting point is 0.0319 cal. per g., the latent heat of fusion is 14.1 cal. per g. The vapor pressure is 10^{-3} mm. of mercury at 540°C., 1 mm. at 840°C., and 100 mm. at 1200°C. The boiling point at atmospheric pressure is between 1440 and 1500°C. The heat of vaporization is 42,700 cal. per gram molecule. The thermal conductivity varies from 0.018 cal./(sec.)(cc. per °C.) at 100°C. to 0.037 at 400°C. and higher. The thermal conductivity of solid bismuth is less than that of any other metallic element except mercury. The mean coefficient of expansion, from 0 to 100°C., is 0.00000731. The viscosity of bismuth is of the same order of magnitude as for cadmium, tin, and lead. The coefficient of viscosity at 23.7°C. is 13.71×10^{8} poises (dynes per $cm.^2$). The surface tension of bismuth is lower than that of tin, cadmium, lead, or antimony. It varies from 376 dynes per cm. at 300°C. to 343.9 dynes at 779°C.

In the electrochemical series, bismuth lies just below hydrogen, together with arsenic, antimony, and copper. From this position, bismuth is positive to such metals as lead and tin. It is less subject to oxidation than lead or tin and more resistant to corrosion under oxidizing conditions. The hydrogen overvoltage at a bismuth surface

[1] Metallurgist, Cerro de Pasco Copper Corp., New York.

[2] *Nat. Bur. Standards Circ.* 382, April, 1930.

in $2N\ H_2SO_4$ at 25°C. is 0.388 volt, somewhat greater than the corresponding value for antimony. Bismuth electrodes show a tendency to passivity in both alkaline and acid electrolytes, and the metal is amphoteric in that it dissolves electrochemically at both anode and cathode.

The specific resistance of solid bismuth is 106.5 microhm-cm. at 0°C., as compared with 1.683 for copper. The mean temperature coefficient of resistance from 0 to 100°C. is 0.00446. Electrical resistance of the solid metal increases with pressure and decreases with tension. At the melting point the specific resistance of solid bismuth is 267 microhm-cm. and of liquid bismuth, 127. Bismuth and antimony are the only two metals whose resistance is greater in the solid than in the liquid state.

Bismuth possesses an unusual thermal e.m.f., about 80 μv per °C. against silver. By coupling pure bismuth with a bismuth alloy containing 5 to 6 per cent tin, an e.m.f. of about 120 μv per °C. can be obtained. A Thomson effect of 676 μv per °C. for an alloy of bismuth with 1 per cent tin, against copper, has been observed. The low melting point and the difficulty of preparing and maintaining wires of suitable size, owing to brittleness and lack of ductility, interfere with the thermoelectric use for bismuth.

Bismuth is the most diamagnetic of all metals, but the susceptibility decreases with rising temperature. An alloy of Cu-Mn-Bi is distinctly magnetic, although all the components are diamagnetic.

The thermal conductivity decreases in a magnetic field. The electrical resistance of bismuth increases when the metal is subjected to the action of a magnetic field.

The absorptive powers of bismuth for X rays have been measured and are similar to those of lead.

Chemical Properties.—Bismuth is not affected by air at ordinary temperature; heated in contact with air, it becomes coated with a grayish-black oxide at temperatures just below the melting point; at higher temperatures a yellow or green oxide (Bi_2O_3) is formed. Bismuth burns with a bluish flame at a bright-red heat, forming Bi_2O_3. Water does not affect bismuth at ordinary temperatures; at white heat, water vapor is slowly decomposed by it.

Bismuth combines directly with chlorine, bromine, and iodine. It is not attacked by dilute sulphuric, dilute hydrochloric, or cold concentrated sulphuric acids; hot concentrated hydrochloric acid attacks bismuth slowly. It dissolves in hot concentrated sulphuric acid and is readily soluble in nitric acid or aqua regia, either hot or cold. Molten bismuth combines directly with sulphur to form bismuth sulphide, Bi_2S_3. Bismuth is precipitated from solution as metal by zinc, manganese, iron, nickel, cadmium, copper, tin, and lead. It is precipitated from solution as the sulphide by hydrogen sulphide and all the soluble sulphides. Basic salts of bismuth are precipitated from solutions of the sulphate, nitrate, and chloride of bismuth upon heavy dilution with water.

Extraction of Bismuth.—Both fire and wet methods, or a combination of both, are used for the extraction of bismuth from ores and metallurgical products. The greater portion of the production is obtained by fire methods. Bismuth produced by either method is generally too impure for use and must be refined.

Extraction by Liquation.—One of the earliest methods to be employed for the recovery of bismuth was liquation. This process was formerly used in Saxony. The liquation was carried out in inclined cast-iron pipes, heated with a wood or coal fire. The ore containing metallic bismuth was introduced into the pipes and the readily fusible bismuth melted and flowed out of the lower ends of the pipes, leaving the gangue of the ore as a residue in the pipes. This residue still contained considerable bismuth, and was drawn from the pipes, smelted to a bismuthic speiss, and then re-treated in the liquation furnace. One form of furnace carried 11 cast-iron pipes, each 4 ft. long.

10 to 12 in. high, and 6 to 8 in. wide; each pipe received a charge of about 33 lb. of ore; 15 to 20 min. were required for the liquation, and the furnace consumed approximately 690 cu. ft. of firewood per 24 hr.

Extraction by Fusion.—The fusion of raw or roasted bismuth ores, with carbon for reduction and the proper fluxes to yield a fusible slag, has superseded the liquation process. The fusion is carried out in either crucibles or small reverberatory furnaces. Metallic iron is added to the charge to decompose any bismuth sulphide in the melt. Lime, soda ash, salt cake, fluorspar, and feldspar are some of the fluxes used to give a fusible slag. The products of the fusion are metallic bismuth, matte, or speiss and slag. The melt is usually cast into molds and the three products separated after solidification. The matte or speiss retains some bismuth and is crushed, roasted, and resmelted. Crucibles made of fire clay and furnace hearths made of firebrick give the best results. The furnace hearth should be removable to permit rapid repairs.

Wet Extraction of Bismuth.—When bismuth is present in ores and metallurgical products as oxide or carbonate, hydrochloric acid is employed to dissolve the bismuth. Metallic bismuth and alloys are treated with nitric acid, aqua regia, or hot concentrated sulphuric acid. A method employed for the extraction of bismuth is as follows: Finely crushed bismuth litharge, cupel bottoms, and other oxidized material containing 5 to 20 per cent bismuth, are treated in stoneware or other suitable vessels with hydrochloric acid. The proportions are 140 to 155 lb. of hydrochloric acid and 22 lb. of water for each 100 lb. of material treated. The mixture is heated gently and stirred for 5 to 6 hr.; water is carefully added until the white bismuth oxychloride just begins to form; it is allowed to settle for 6 to 8 hr., and the clear solution is then siphoned into wooden tanks. Water is added to this solution in order to complete the precipitation of the bismuth oxychloride, and the mixture is allowed to settle. The clear liquor is siphoned off and is treated with scrap iron to precipitate any copper carried by the solution. The bismuth oxychloride is washed with hot water to remove as much lead chloride as possible, then dissolved in hydrochloric acid and reprecipitated by dilution with water. It is then filtered, dried, and smelted with lime and charcoal to metallic bismuth. The bismuth produced by this method usually contains small amounts of lead, silver, and other impurities. The leach residue, containing lead, silver, and other metals, is washed, filtered, dried, and mixed with lime or soda ash and carbon, reduced to metal, and reworked in the cupel furnace for the recovery of the silver and other values.

Electrolytic Refining.—Bismuth can be refined electrolytically. Both the chloride and the fluosilicate electrolytes have been used. The more economical fire-refining methods have largely replaced electrolytic refining.

Separation of Bismuth from Lead Bullion.—Substantially all the bismuth production of the Western Hemisphere is derived from flue dusts from copper-smelting operations or from lead ores. The bismuth-bearing dusts are generally treated at lead-smelting plants, in which case the bismuth is collected in the lead bullion.

Bismuth can be separated from lead bullion by the following methods:

1. Electrolytic refining of the lead bullion (Betts process)
2. Betterton-Kroll process.
3. Crystallization (Pattinson or Hall processes).
4. Electrolytic production of white lead (Sperry process).

In the electrolytic refining process, the lead bullion is cast as anodes and refined to very pure lead cathodes and an anode residue or slime from which the bismuth is recovered.

The slime is melted and arsenic, antimony, and more or less of the lead are removed by selective oxidation, leaving a metal containing gold, silver, copper, bismuth, tellurium, and some lead. This metal is treated by further oxidation to yield doré

and a bismuth-copper-lead-tellurium slag. The slag is reduced with carbon to a crude bismuth metal. If present in excess, copper and tellurium can be collected in a matte by the addition of sulphur to the melt. Salt cake and carbon, galena, or pyrite are sometimes used in place of sulphur. If the crude bismuth contains large amounts of tellurium, it is removed by successive treatments with molten caustic soda. The crude bismuth is then drossed by cooling and skimming for the further elimination of copper and tellurium. Silver, gold, and residual copper and tellurium are eliminated by zinking and skimming. The desilverized bismuth is refined with chlorine gas. When the lead has been eliminated, the residual chlorine is removed from the metal with air and the bismuth is given several treatments with molten caustic soda before casting. The refined metal should assay 99.995 per cent bismuth. All drosses and skims from the refining operations are re-treated for recovery of valuable metals.

In the Betterton-Kroll process the lead bullion is softened and desilverized by standard Parkes process methods. The desilverized lead is treated with metallic calcium or calcium and magnesium, cooled, and the calcium-bismuth dross removed. The residual calcium and magnesium in the lead are removed with chlorine or molten chlorides before casting as refined lead. The calcium-bismuth skims are treated with chlorine or molten chlorides for removal of calcium and magnesium. The crude bismuth is refined as outlined above.

Crystallization, by the Pattinson or Hall process, is not used today, except to supplement the chlorine refining of crude bismuth or in re-treating some of the products from dross and skims.

The Sperry process for production of white lead employs anodes of lead bullion, producing an anode slime which is treated for the recovery of silver, gold, and bismuth, as in the electrolytic refining of lead.

Current Production.—The current production of bismuth in the Western Hemisphere is estimated to be between 2,500,000 and 3,000,000 lb. per year. The principal producers are: the American Smelting & Refining Co., the Cerro de Pasco Copper Corp., the Consolidated Mining & Smelting Co. of Canada, Ltd., the International Smelting & Refining Co., the U. S. Smelting, Refining & Mining Co. The New York quotation for refined bismuth has been $1.25 per pound since October, 1939.

Uses.—The principal use of bismuth for many years was in the production of pharmaceutical compounds. During the last ten years, however, the industrial and engineering uses of bismuth and its low-melting alloys have expanded rapidly. The addition of small amounts of bismuth and lead to some of the strong aluminum alloys is used to render the alloys free cutting. The addition of fractional percentages of bismuth to the so-called stainless steels and to the manganese steels improves the machinability of these steels.

Bismuth is a constituent of a number of eutectic alloys, some of which are:

Melting temperature		Composition				
°F.	°C.	Bi	Pb	Sn	Cd	Others
116.6	46.8	44.70	22.60	8.30	5.30	In 19.10
158.0	70.0	49.41	27.67	12.88	10.02	
196.7	91.5	51.65	40.20	.....	8.15	
203.0	95.0	52.00	32.00	16.00		
216.5	102.5	53.90	25.90	.....	20.20	
255.7	124.3	55.50	44.50			
266.0	130.0	56.00	.....	40.00	.....	Zn 4.00
281.3	138.5	57.00	.....	43.00		
291.0	144.0	60.00	.....	.....	40.00	

The eutectic alloys are not satisfactory for many applications, because of their very narrow freezing ranges. Many alloys having wide freezing ranges have been developed. Some of the fusible alloys expand during solidification, some shrink, while others grow rapidly in the solid state after solidification. One alloy composed of bismuth, lead, tin, and cadmium shrinks during solidification; further shrinkage occurs on cooling from solidification temperature to room temperature, when it begins to grow. The growth is very rapid for about 10 to 12 hr. Approximately 95 per cent of the total growth occurs in the first 12 hr., and this growth almost exactly compensates for the shrinkages that occur during solidification and cooling of the alloy. The alloys that grow in the solid state are in general harder in the aged condition than when first cast.

Bismuth alloys are employed in:

Safety plugs for compressed-gas cylinders and tanks.

Fusible elements in automatic sprinkler heads, fire-door release links, automatic shut-offs for electric and gas water-heater systems.

Constant-temperature baths for autoclaves.

Liquid seals for bright-annealing and nitriding furnaces.

Low-melting solders.

Forming dies in aircraft construction.

Spotting, erection, and checking fixtures for aircraft construction.

Bending thin-wall tubing and molding.

Production of accurate patterns.

Cores on which copper, iron, and other metals are electroformed.

Anchoring dies, punches, machine parts, magnets, and ceramic parts.

Chucks for holding irregular or delicate articles during machining operations.

Spray coating for wood patterns, core boxes, etc.

Models for engraving machines.

Proof casting of forging dies, plastic molds, and other irregular cavities.

Selenium rectifiers.

CHAPTER VII

LEAD

By R. G. Bowman[1]

Nature and Uses.—Lead is the heaviest and softest of all the common met It has a specific gravity of 10.37 to 10.65 (molten); 11.35 to 11.37 (solid); it is, in it pure metallic state, so soft as to be readily scratched by the fingernail, while it easil marks paper with a gray streak. Only the pure metal exhibits this degree of softne many commercial grades containing small amounts of antimony, arsenic, copper, and zinc being distinctly harder. The degree of hardness increases with the amount of impurity present. The metal has a dull bluish-gray color, is malleable but not ductile. Its tensile strength is low, 2600 to 3300 lb. per sq. in.; its elastic limit is 0.5 lb. The tensile strength is about two and one-half times the tenacity. Lead is not sufficiently ductile to be drawn into fine wire.

Lead melts at 327.4°C., boils at about 1525°C. (at 760 mm.), but does not readily distill. If, however, a mixture of zinc and lead is subjected to distillation at a high temperature, the zinc vapor carries over with it a considerable quantity of lead vapor; and hence the source of part of the losses in lead smelting. Lead is somewhat volatile when heated to a cherry red with access of air.

Commercial Grades of Lead.—The commercial grades of refined lead as established by the A.S.T.M. are shown in Table 1.

Uses of Lead.—Lead is used (1) in the form of refined metal, (2) as a base for alloys with other metals, (3) in the form of chemical compounds.

The proportion of lead consumed in various applications is shown in Table 2.

In smelting, lead is used as a collector for other metals, particularly for gold and silver, from which it is later separated, generally by use of zinc in the Parkes process of desilverization.

Lead alloys readily with most of the nonferrous metals and forms the base for a large number of important industrial alloys. The principal types of lead-base alloys are: type metal, bearing or babbitt metal, shot, solders, casting metals, leaded brasses, and fusible alloys used for the protection of electrical apparatus, in automatic sprinklers, etc. From 0.1 to 0.2 per cent arsenic is added to lead used in making shot to increase the hardness and sphericity of the product. Antimony imparts the quality of hardness essential to some ammunition and the property of expansion on solidification essential in type metal and casting metals generally. Bearing metals comprise alloys of lead and antimony, or these together with copper, tin, and zinc. The addition of lead to brass produces an alloy that is soft and machines easily. Solder is commonly an alloy of lead and tin; the melting point varies with the proportion of these constituents and others, sometimes added for special purposes. Commercial solder ranges in composition from 3 to 60 per cent tin, the remainder being lead. The alloy of 1 part tin and 3 parts lead melts at 452°F., tin alone melting at 442°F. With increase of tin content to 56 per cent the fusion point is lowered to 345°F., then rises to 352°F., with further increase to 75 per cent tin. In practice, therefore, solder

[1] General superintendent, International Smelting & Refining Co., East Chicago, Ind.

In the preparation of this chapter the former chapter by Mr. G. C. Riddell was drawn upon freely. Figures 3, 4, 44–60, and 65 are from Vol. 121, *Trans. A.I.M.M.E.*, by permission.

seldom contains more than 50 per cent tin. The addition of bismuth, cadmium, or mercury lowers the melting point below the boiling point of water. The low-fusion-point alloys of this type have many commercial uses.

The most extensive single application of a lead-casting alloy is in the manufacture of storage-battery grids which are made of an alloy of 6 per cent antimony and 94 per cent lead.

Type metal has a wide range of composition, *e.g.*, 50 to 80 per cent lead, 2 to 35 per cent tin, and 5 to 30 per cent antimony. Some also contain nickel, copper, and bismuth.

TABLE 1.—STANDARD SPECIFICATIONS FOR PIG LEAD[1]

Tentative specifications for pig lead published since 1919, and last revised in 1940 by the American Society for Testing Materials (A.S.T.M. Designation B 29-40) cover refined lead in pig form made from ore or other material by processes of reduction and refining, and exclude lead reclaimed by simple melting, drossing, and casting. The requirements as to chemical composition are as follows, in percentages:

	Corroding lead	Chemical lead	Acid lead	Copper lead	Common desilverized lead A	Common desilverized lead B	Soft undesilverized lead
Silver, max	0.0015	0.020	0.002	0.020	0.002	0.002	0.002
Silver, min	....	0.002					
Copper, max	0.0015	0.080	0.080	0.080	0.0025	0.0025	0.04
Copper, min	....	0.040	0.040	0.040			
Silver and copper together, max	0.0025						
Arsenic, max	0.0015						
Antimony and tin together, max	0.0095						
Arsenic, antimony, and tin together, max	....	0.002	0.002	0.015	0.015	0.015	0.015
Zinc, max	0.0015	0.001	0.001	0.002	0.002	0.002	0.002
Iron, max	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Bismuth, max	0.05	0.005	0.025	0.10	0.15	0.25	0.005
Lead (by difference), min.	99.94	99.90	99.90	99.85	99.85	99.73	99.93

[1] American Bureau of Metal Statistics, 1941.

Corroding lead is a designation that has been used for many years in the trade to describe lead which has been refined to a high degree of purity.

Chemical lead has been used for many years in the trade to describe the undesilverized lead produced from Southeastern Missouri ores.

Acid lead is made by adding copper to fully refined lead.

Copper lead is made by adding copper to fully refined lead.

Common desilverized leads A and B are designations that are used to describe fully refined desilverized lead.

Soft undesilverized lead is used in the trade to describe the type of lead produced from ores of the Joplin, Mo., district.

One of the most valuable properties of lead is its resistance to corrosion, though its physical weakness is a disadvantage in many mechanical operations. The addition of comparatively small amounts of some other metals greatly increases its mechanical strength without impairing its corrosion resistance and other valuable characteristics.

TABLE 2.—USE OF LEAD IN THE UNITED STATES[a]
(In tons of 2000 lb.)

Purpose	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943
White lead	64,500	80,000	85,500	86,000	71,000	75,000	65,500	85,000	75,000	50,000
Red lead and litharge[b]	42,000	47,500	54,000	57,000	43,000	57,200	59,400	89,100	68,000	79,000
Storage batteries	163,000	175,000	191,000	192,000	167,000	198,000	220,200	245,000	215,600	257,000
Cable covering	35,200	38,900	61,400	90,000	60,000	74,400	107,400	173,000	165,000	132,000
Building[c]	30,000	32,000	40,000	45,000	36,000	50,000	65,000	95,000	110,000	62,000
Automobiles	7,300	10,000	11,100	12,000	6,000	8,900	11,000	12,000	3,000	1,000
Ammunition	34,800	29,200	32,500	39,500	31,200	42,300	56,000	71,500	83,000	178,000
Terne plate	2,600	4,700	6,200	6,400	4,300	6,000	6,000	8,700	4,900	5,000
Foil	16,200	15,900	28,500	21,700	22,000	21,800	23,500	45,000	7,700	13,000
Bearing metal	12,100	13,000	16,500	15,000	9,000	12,800	14,000	25,000	20,000	23,000
Solder	16,000	20,000	22,000	22,000	15,000	20,000	24,000	36,000	38,000	38,000
Type metal	13,000	15,000	17,000	17,000	12,000	14,000	16,800	20,000	20,000	17,000
Calking	10,000	12,000	13,500	15,000	12,000	16,000	19,200	31,000	40,000	30,000
Castings	5,000	5,000	5,750	6,000	6,000	7,500	9,000	14,000	[e]	[e]
Other uses[d]	36,300	40,700	48,600	54,100	51,500	63,100	85,000	99,700	149,800	215,000
Totals	488,000	538,900	633,550	678,700	546,000	667,000	782,000	1,050,000	1,000,000	1,100,000

[a] Includes antimonial lead.

[b] Exclusive of oxides for storage batteries.

[c] Under the head of building is included the lead used in chemical construction.

[d] Among "other uses" the largest item in recent years has been the manufacture of lead tetraethyl for tempering gasoline. Also included are lead for brass making, collapsible tubes, lead-lined pipe, lead-headed nails, railway equipment, shipbuilding, and many miscellaneous uses. The figures for 1942–1943 include lead exported.

[e] Included in "other uses."

NOTE: We estimate that about 75 per cent of the lead that goes into storage batteries returns into production of soft and hard lead, which production is not accounted for fully in the usual tables owing to omission of most of the secondary smelters. For this reason the totals in the above accounting are in excess of shipments reported ex-primary refineries.

In the accounting for the use of lead in 1941 the allocation to ammunition does not include the use for that purpose in the government arsenals, and also omitted are consignments of refined pig lead for governmental use otherwise. Table and notes by courtesy of American Bureau of Metal Statistics.

Commercial grades of lead containing such additions are not usually classed as alloys, owing to the small amount of metal other than lead.

The most important commercial grade of this type is that containing 0.04 to 0.06 per cent copper, which is widely used for protective sheathing on electric cables and for chemical-plant equipment. Other important grades are tellurium lead, containing about 0.05 per cent tellurium, and calcium lead, containing 0.02 to 0.05 per cent calcium.

The addition to steel of up to 0.50 per cent lead produces an important increase in machinability.

Alloys of Lead.—The compositions of some of the leading industrial alloys of lead are given in Table 3.

The largest use of lead in the form of a chemical compound is in the field of pigments. The most important of these is white lead, a basic carbonate, $2PbCO_3$-$Pb(OH)_2$, used alone or as a base for mixed paint. Red lead, Pb_3O_4, is used as a rust-inhibitive priming coat for iron or steel. Lead basic sulphate, known as sublimed white lead, and lead chromate are also important lead pigments.

Litharge, PbO, is used in large amounts in the manufacture of storage batteries, in rubber compounding, and in the manufacture of glass and ceramic glazes. Lead borate is used in ceramics; lead arsenate is an insecticide; and lead acetate and other compounds are used in medicine.

History.—Lead is one of the six so-called prehistoric metals. The oldest people of whom there is any record, the Egyptians, used lead in glazing pottery, and the abundance of silver among the ancients must have been derived from argentiferous lead ores in various places. Among the Egyptians, gold, silver, and lead came into use, together, in the period 7000 to 5000 B.C. One of the oldest pieces of lead in existence is a figure in the British Museum which antedates 3800 B.C. Lead was known and used by the Chinese before 3000 B.C. The Phoenicians worked the Rio Tinto deposit about 2000 B.C. The mines at Laurium, Greece, reopened by a French company in 1863, flourished in the fifth century B.C. In the third century B.C. the Romans operated the lead mines in Spain, the same deposits that today form one of the major districts of the world.

About the period A.D. 700 to 1000, the German lead-silver mines in the vicinity of the Rhine and the Hartz Mountains were opened, and in A.D. 1200 those in Saxony, Silesia, and Bohemia. Lead mining in the United States, now the leading producing country of the world, dates back to the beginnning of the seventeenth century (1621) when lead was mined and smelted in Virginia. The lead ores of the United States came from the Mississippi Valley between 1700 and 1867, in which latter year the first great mines of the West were opened. The Mississippi Valley ores are non-argentiferous, *i.e.*, they do not contain enough silver to pay for its extraction. The ores of the Western states are argentiferous and in most instances are quite complex in composition.

The manner in which prehistoric people extracted lead from ore is unknown, but it is readily imagined that primitive furnaces, small pits dug in the ground or in the hillsides, enclosed by stones to form a small shaft, provided early equipment for the recovery of lead from oxide and sulphide ores heated with charcoal. Blast, to produce the temperature required for forming slag, must have been applied by reed and bellows. The furnaces found in Sinai in which copper ores were smelted about 4000 B.C. had this form: a cavity 30 in. deep, a side wall 26 in. high, and with two tuyère openings; the furnaces at Laurium were similar. At Bawdwin, Burma, the remains of the ancient lead-silver smelting and refining furnaces show this same crude Scotch-hearth effect. These Burma furnaces have no iron work of any kind in or around them. They are simply an excavation in the side of the hill, semicircular in horizontal cross-

section; the radius at the top is 2 ft., tapering to about 9 in. at the sump. The depth from the top edge of the furnace to the bottom of the sump is between 5 and 6 in. Back of the clay lining of the sides are three 3-in. square air passages extending from the top edge to the level of top of sump. The operation of these primitive furnaces was undoubtedly similar to that followed in the modern Scotch hearth. Similar contrivances, the log furnace and the ash furnace, were used in smelting ores in the

TABLE 3.—LEAD-BASE ALLOYS

Name	Pb	Sb	Sn	
Type metal:				
Best	50	25	25	
German	75	23	2	
	70	18	10	Cu, 2
Common	60	30	10	
French	55	30	15	
Linotype (American)	85	12	3	
Bullets (shrapnel)	94	6		
Engraving plate	60	40		
Pewter:				
Usual	20	80		
French	18	82		
Bearing metal:				
Atlantic Coast Line	85	15		
Pennsylvania R.R.	87	13		
Baltimore & Ohio R.R.				
Thin linings	94–96	3–5	0.5–1.5	
Thick linings	86	10–12	3–5	
Chicago & Eastern R.R.	84–85	12–14	2	
Chesapeake & Ohio R.R.	91.5	7	1.5	
Magnolia metal	79.75	15	5	Bi, 0.25
Solder:				
No. 1, tinman's	34		66	
No. 2, half and half	50		50	
No. 3, plumbers'	66		34	
Cable sheathing[a]	98.0 99.2		2.0 0.8	
Frary metal (Ulco)	97+			Ca 1 Ba 2
White metal, or antifriction bearings:				
Heavy load	87	7	6	
Jacoby metal	85	10	5	
Jacoby metal	62	10	27	
French R.R. (Cie. de l'Est)	80	8	12	
French R.R. (P.-L.-M. R.R.)	70	10	20	
Ship shaft bearing	72	7	21	
Shot	99.5–99.8			As, 0.2–0.5
Terne metal	80.25	1.75	18	

[a] Special leads used for cable sheathing contain Cu, Sb, or Ca in amounts less than 0.10 per cent and are not ordinarily classed as alloys. The most important one of these contains 99.85 per cent Pb and 0.06 per cent Cu.

Mississippi Valley about 1720. In 1836 the first Scotch hearth was erected in this country. This furnace had been in operation in England since 1730.

Chemical Properties.—Lead is tetravelent; its atomic weight is 207. It tarnishes rapidly in moist atmosphere, although its surface undergoes no change in perfectly dry air, or in water that is free from air. If melted in contact with air, it oxidizes, with a coating of iridescent pellicles of suboxide which, at dull red heat, are converted into PbO. If the heating is continued at a temperature of 400 to 430°C., the PbO gradually changes to red oxide (Pb_3O_4), which dissociates into 3PbO and O at 550°C. The other oxides that lead forms are the sesquioxide, Pb_2O_3, and the peroxide, PbO_2. All oxides with more O than PbO are decomposed into PbO and O at 630°C.

The best solvent of lead is nitric acid, the very dilute acid acting more rapidly than the strong. Dilute hydrochloric and sulphuric acid have little effect on lead, these acids forming coatings of $PbCl_2$ and $PbSO_4$ which protect it further from action. Up to 200°C.—the highest temperature employed under normal conditions in acid concentrating practice—pure lead is but little attacked by strong HCl or by the pure or nitrous sulphuric acid, but above 200° the action becomes stronger, and at 260°C. lead is completely dissolved. Boiling concentrated HCl and H_2SO_4 attack the metal slowly, even in large masses, and dissolve it with fair rapidity if it is in a finely divided condition. Nitrous sulphuric acid acts upon lead at all temperatures more readily than does the pure acid. Acetic, citric, tartaric, and other organic acids act upon it slowly in contact with moist air. It is attacked by SO_2 between 550 and 850°C., and is also acted upon by HF, but the dissolution in hydrofluoric acid is quickly checked by the formation of PbF_2; hence the acid can be stored in lead vessels.

The compounds of lead are poisonous practically in proportion to their solubility; the metal itself and its sulphide, being incapable of absorption as such into the system, are almost innocuous, while the soluble salts, chloride, nitrate, acetate, etc., are active irritant poisons. The oxide, sulphate, and carbonate are less active, but continued exposure to lead fume, or to any atmosphere in which these substances are present in the form of dust, is dangerous and will result in lead absorption or "plumbism." This condition is entirely curable and can be entirely prevented by adequate ventilation of working places, the use of respirators, protective clothing, and personal cleanliness. By reason of such measures and careful medical inspection, modern lead industries offer no greater hazards to the worker than do most other industrial fields.

Lead Compounds.—The more important compounds of lead and the chemical reactions that are of importance in the extraction of the metal are as follows:

Lead Oxide, PbO.—This is the oxide of greatest metallurgical importance. It occurs in two forms—massicot and litharge. Massicot is an amorphous yellow powder produced by heating lead on flat hearths at a full red heat, continually removing the film of suboxide, and oxidizing it to the yellow oxide at a low temperature, avoiding fusion. On raising the temperature to a bright red heat, this oxide melts and, on cooling, solidifies as crystalline litharge. Litharge is obtained on a commercial scale by cupeling refined lead and collecting the oxide as a skimming or a fume. The melting point of litharge is 883°C.; it is volatile in air below 900°C. It is a good conductor of electricity when molten.

Toward acid furnace materials, litharge is a strong base, quickly corroding them by forming lead silicates. It is an excellent flux, forming fusible compounds with oxides that are infusible alone, such as CaO, BaO, MgO, and Al_2O_3. These bases do not always enter into chemical combinations with PbO, but are simply held in fused solutions by an excess of litharge. In the case of the metallic oxide CuO, 1 part of CuO forms a fusible mixture with 1.8 part of PbO. No chemical compound occurs, but there is a eutectic with 32 per cent CuO freezing at 689°C. This explains the

fact that, in cupeling, coppery litharge flows more readily than litharge free from copper. Litharge readily gives up its oxygen. Sulphur, tellurium, arsenic, antimony, tin, copper, zinc, and iron are wholly or partly oxidized when melted with litharge, the oxides being either volatilized or slagged by the surplus of litharge.

Reduction of PbO by carbon begins at 400 to 500° and is vigorous at 700°C. Reduction by carbon monoxide begins at 160°, by hydrogen at 235°C. Heated to bright redness with lead sulphide, in the proportion of two molecules of litharge to one of sulphide, all the lead in both compounds is reduced to metal, and sulphur dioxide is evolved, according to the equation

$$PbS + 2PbO = 3Pb + SO_2 - 52{,}540 \text{ cal.}$$

Minium or Red Lead, Pb_3O_4.—This is a combination of 2PbO and PbO_2, a bright red powder prepared by heating a mixture of PbO_2 and PbO at about 250°C

$$2PbO + PbO_2 = Pb_3O_4$$

Lead Peroxide, PbO_2.—This is a powerful oxidizing agent, detonating with phosphorus. It is used in the manufacture of matches and in storage batteries, in which latter it is repeatedly destroyed and reformed during the operation of discharging and recharging.

Lead Carbonate, $PbCO_3$, *and White Lead*, $2PbCO_3.Pb(OH)_2$.—Lead carbonate occurs in nature as cerussite. At 200°C. it decomposes into PbO and CO_2, and at the same temperature is reduced to metallic lead by CO. The white lead of commerce is a hydrated basic carbonate. This pigment has for centuries been prepared by the "Dutch" or "corroding" process which, briefly stated, consists in the slow corrosion of lead by the vapor of acetic acid and the conversion of the corroded material into hydrated carbonate of lead by CO_2 generated from decomposing organic matter. The process is tedious, taking over 90 days to complete. The lead is cast into "buckles," which, exposing maximum surface to corrosion, are placed in clay pots containing dilute acetic acid or vinegar. The pots are stacked in tiers and covered with tanbark. The carbon dioxide required for the ultimate conversion of the corroded lead is generated by the fermentation of the bark. The white carbonate is cleaned from the buckles in revolving drums and the impurities are separated by flotation, washing and screening before it is dried and packed for shipment or is ground in oil for use. From 125 to 129 lb. of white lead should be obtained from 100 lb. of metal.

A considerable proportion of white lead is still produced by this process, which gives an excellent pigment. More modern processes reduce the time required, afford better opportunities for control of the composition and physical characteristics of the product, and yield a product that requires no further purification. The principal processes in use are the following:

Carter Process.—Finely divided metallic lead is treated with acetic acid and carbon dioxide in revolving wooden drums. The lead is completely converted into basic carbonate in 8 to 12 days and is washed, dried, and pulverized.

Euston Process.—Metallic lead is dissolved in acetic acid as basic lead acetate and precipitated as basic carbonate with carbon dioxide.

Sperry Electrolytic Process.—Pure basic carbonate of lead is produced in a bifluid electrolytic cell having a lead anode and a steel cathode, separated by a linen diaphragm. The two electrolytes are sodium acetate solutions differing in carbonate-ion concentration. The lead dissolves at the anode, is reprecipitated as basic carbonate in suspension in the anolyte, and flows continuously from the cell in this suspension as the anolyte is circulated. It is removed by settling and filtration and is dried, pulverized, and packed. The catholyte acts as a feeder to maintain an exact concentration of the anolyte through electrolytic control. The purity of the

product is independent of the purity of the anode lead, since only the lead dissolves. The process affords an opportunity for complete control of the composition and physical characteristics of the product at all times and produces an extremely pure and brilliantly white pigment.

Sublimed White Lead (Basic Lead Sulphate).—This is a white pigment, ranging in composition from pure $2PbSO_4.PbO$ to 75 per cent $PbSO_4$, 20 per cent PbO, and 5 per cent ZnO and is largely produced directly from lead ore, whereas the basic carbonate (white lead) is made almost exclusively from metal. Basic lead sulphate is used extensively in paint and in the manufacture of oilcloth, paper, and rubber goods. The raw material used in its manufacture is silver-free galena from the Missouri field. This is ground fine, mixed with carbon (and gray slag from the ore hearth), and smelted in an oxidizing atmosphere. The pigment is collected in baghouses. Blue fume, or "sublimed blue lead," is a by-product of the process and is used in the same industries as is the major product. Sublimed blue lead consists of 50 to 53 per cent $PbSO_4$, 41 to 38 per cent PbO, with small proportions of PbS, $PbSO_4$, ZnO, and carbon.

Lead Silicates.—Lead silicates are much used for glazing tile, pottery, etc. Lead oxide and silica begin to combine at the softening temperature of the oxide, *i.e.*, below 800°C. The silicates do not give up their lead readily, the ordinary reducing agents sulphur and carbon decomposing them with difficulty. Iron in excess effects the decomposition of lead silicates at bright-red heat, forming monosilicates ($2FeO.SiO_2$). FeS throws down some Pb, a double silicate of lead and iron being the result.

Lead Sulphide, PbS.—This occurs in nature, as galena, and can be artificially prepared by melting sulphur and lead, or by adding hydrogen sulphide to a solution of a lead salt. It is produced in smelting lead ores as a sublimate on the cooler part of the furnace walls. PbS melts at about 1120°C. to a thin fluid which penetrates the firebrick of the furnace; furnace linings usually contain a network of crystalline galena. It volatilizes at temperatures below its melting point. Sublimed galena constitutes a large portion of the accretions on the shaft walls of lead blast furnaces.

Being isomorphous with Ag_2S, Cu_2S, ZnS, FeS, etc., lead sulphide readily mixes with these sulphides in all proportions, forming the mattes obtained in smelting complex sulphide ores. Galena is decomposed by fusion with iron, the reaction forming the basis of what is known as the "precipitation" process of lead smelting.

$$PbS + Fe = Pb + FeS, \qquad \text{or} \qquad 4PbS + 4Fe = 3Pb + PbS + 3FeS + Fe$$

Lead sulphide is decomposed by those metallic elements which have a stronger affinity for sulphur than lead, in the following order:

Mn—Cu—Ni—Fe—Sn—Zn

manganese forming the strongest and lead the weakest sulphide. In the smelting of lead ores, manganese does not have to be considered in this connection, as it is usually present as MnO_2, which enters the slag and hence is found only in small amount in the matte.

In smelting practice, the decomposition of PbS is never complete. It is customary to calculate the iron necessary for the decomposition of PbS in accordance with the formula $Fe + PbS = Pb + FeS$; if less iron is added, the resulting matte remains too rich in lead, while if an excess is supplied it simply goes into solution in the PbS-FeS matte. An excess of iron in the charge, while often advantageous in cutting out crucible crusts, may be disadvantageous in decomposing argentiferous galena, since, owing to the affinity of Ag_2S and FeS, more silver will be drawn into the matte than can be accounted for by the amount of lead present. In addition to having the correct amount of iron present to decompose PbS, it is important to have the temperature as high as possible, within reasonable limits.

A basic ferrous silicate, $4FeO.SiO_2$, will decompose PbS readily; the single silicate, $2FeO.SiO_2$, has little effect. CaO and BaO have, in the presence of carbon, a decomposing action on PbS.

$$2PbS + CaO + C = Pb + (PbS.CaS) + CO$$

Lead Sulphate, $PbSO_4$.—This occurs in nature as anglesite and is formed in roasting PbS and in precipitating lead salts with H_2SO_4. It is the most stable of all sulphates of the heavy metals, remaining unaltered at a bright-red heat. At 800 to 1000°C., it dissociates, fusion also occurring between 950 and 1000°C.

Silica decomposes $PbSO_4$ at 1030°C. in accordance with the equation

$$2PbSO_4 + SiO_2 = 2PbO.SiO_2 + 2SO_2 + O_2$$

this reaction being the basis of "slag roasting." This decomposition by silica is governed by the viscosity of the lead silicates formed, the viscous slag enveloping $PbSO_4$ and blocking the action. According to Mostowitsch, the most rapid decomposition and the lowest loss of lead by volatilization lies between the singulo- and bisilicate containing 10 to 15 per cent SiO_2.

Fe_2O_3 also has a decomposing effect on $PbSO_4$, though in less degree than SiO_2. FeO, above 800°C., is oxidized by some of the O from $PbSO_4$. Iron at high temperature is both oxidized and sulphurized: $4Fe + PbSO_4 = Fe_3O_4 + FeS + Pb$; calcium is sulphatized: $CaO + PbSO_4 = CaSO_4 + PbO$; and metallic lead is oxidized: $Pb + PbSO_4 = 2PbO + SO_2$.

Carbon and carbon monoxide reduce lead sulphate to PbS, with the formation, also, of Pb and SO_2. This double reaction explains the disappearance of S as SO_2 in the reducing fusion of a lead blast furnace. In smelting the gray slag from the ore hearth, as much as 50 per cent of the sulphur is usually expelled.

Reactions between Lead Oxide, Sulphide and Sulphate.—Intimate mixtures of PbS and PbO, and of PbS and $PbSO_4$, such as exist in the roasting and smelting of lead ores, react in accordance with the following equations to form metallic lead and SO_2:

$$PbS + 2PbO = 3Pb + SO_2 - 52{,}540 \text{ cal.}$$
$$PbS + PbSO_4 = 2Pb + 2SO_2 - 97{,}380 \text{ cal.}$$

These two equations form the basis of the roasting and reaction or air-reduction process. Except for the fact that the gaseous product SO_2 is withdrawn from the furnace as fast as formed, both these reactions would reverse and equilibrium result.

If there is an excess of PbS or PbO over that called for by the equation, the excess remains unaltered. If there is an excess of $PbSO_4$, part or all of the lead is obtained as PbO.

$$PbS + 3PbO = 3Pb + PbO + SO_2$$
$$2PbS + 2PbO = 3Pb + PbS + SO_2$$
$$PbS + 2PbSO_4 = Pb + 2PbO + 3SO_2$$
$$PbS + 3PbSO_4 = 4PbO + 4SO_2$$

Plumbites and Plumbates.—The oxides PbO and PbO_2 form plumbites and plumbates with alkali, alkali earths, and some metallic oxides. The orthoplumbate, Ca_2PbO_4, occurs in the blast roasting of lead sulphides with lime diluents.

Lead Ferrite.—The fact that in the crucible assay for lead the presence of Fe_2O_3 acts unfavorably on the yields of lead is believed due, in part at least, to the formation of ferrite compounds, one of these having the formula $PbO.FeO.4Fe_2O_3$. The melting point of PbO is lowered 133°C. by the addition of 12 per cent by weight of Fe_2O_3.

Lead Chloride.—This is formed by the action of chlorine upon lead and in a chloridizing roast of lead and its compounds. The volatility of $PbCl_2$ is the basis of a process

for the extraction of lead from its ores, the chloride volatilization process, in which the chloride fume is precipitated by being passed through an electrostatic precipitator. The solubility of $PbCl_2$ in saturated sodium chloride liquor is also the basis of another process of lead recovery, the brine-leaching process, in which sulphide ores roasted in contact with sodium chloride are dissolved by strong brine solutions, out of which the lead is precipitated either electrolytically or on scrap and sponge iron.

Lead Selenide and Telluride (*PbSe and PbTe*).—These occur as clausthalite and altaite and are formed by the direct union of components. They are readily decomposed by roasting. Selenides and tellurides are found in the anode mud formed in the electrolytic refining of copper and lead, this mud being the raw material for the production of selenium.

Lead Borates.—Lead oxide and boric trioxide melt together in all proportions, and the compounds formed are more fusible than the corresponding silicates. Advantage is taken of this fact in lead and silver assaying by the use of borax as a flux. Lead borates are used in the preparation of ceramic glazes.

Lead Fluosilicate, $PbSiF_6$.—This is formed by the action of H_2SiF_6 on PbO when some SiO_2 is precipitated. A solution containing about 8 per cent $PbSiF_6$ and 11 per cent free H_2SiF_6 is used as electrolyte in the electrolytic refining of lead.

Lead Ores.—Lead and zinc are commonly associated in mineral deposits, sometimes intimately mixed, sometimes sufficiently segregated so that one metal predominates, but seldom free entirely from the other. The geological and geographical distribution of the two metals is, therefore, nearly identical.

All lead ores contain substances other than lead minerals. Some of these substances (*e.g.*, gold, silver, or copper) can be recovered in the smelting process and may add much to the value of the ore. The common impurities in lead ores are silica, iron, lime, barytes, zinc, antimony, and arsenic. The first three (in minor amounts) may be beneficial or detrimental in any given ore, depending upon whether the bulk of the ore supply of the smelter carries an excess of one or the other of these elements which, in proper proportions, are required in the smelting operation. On the other hand, zinc and, to a less extent, antimony are always detrimental and detract from the value of the ore unless separated from the lead before shipment to the smelter. Sulphur, a constituent element of galena, is not considered a deleterious element except that carbonate ores of similar grade are more valuable, since they are cheaper to smelt. Barytes and other less common constituents of lead ores, including traces of valuable metals (bismuth, cadmium and rare elements), are seldom present in quantities sufficient to affect the value of the ore to the miner.

The more common ore minerals of lead are the following:

Mineral	Formula	Percentage of lead
Galena.......	PbS	86.4
Cerussite.....	$PbCO_3$	77.5
Anglesite.....	$PbSO_4$	68.3
Pyromorphite	$3Pb_3P_2O_8.PbCl_2$	76.3
Wulfenite....	$PbMoO_4$	56.3
Jamesonite...	$PbSb_2S_5$	34.1

Galena is the most common and important of these minerals. The next three minerals in the list usually result from the surficial oxidation of galena, the sulphate being usually an intermediate stage in the oxidation to the carbonate. Pyromorphite

and wulfenite are of minor importance. Jamesonite is considered more an ore of antimony than of lead.

Sphalerite weathers more readily than galena and zinc, therefore it is often carried below water level more rapidly and completely than lead. This fact accounts for some mines changing from predominantly lead mines to zinc mines with greater depth. Apart from the effect of such secondary enrichment, this change is often encountered in primary ores with increase in depth.

Important types of lead deposits are as follows:

1. Deposits formed at shallow depth in sedimentary rocks without apparent connection with igneous rocks. These have evidently formed under conditions of temperature and pressure approximating those of the present surface. They occur as tabular replacements of receptive strata usually in limestones and dolomites, but sometimes in quartzites or cherts and conformable with the enclosing strata; also as irregular masses along faults, in zones of brecciation, in fissures, joints, crevices, and cavities erratically distributed in the same rocks.

In regions of slightly disturbed strata the ore shoots tend to follow pitching troughs. The ores of this type usually contain lead (galena), zinc (sphalerite), and iron (pyrite) minerals; often manganese and cadmium; sometimes cobalt and nickel; but seldom gold, silver, copper, or antimony.

The deposits of this type are of worldwide distribution and are often extensive and commercially important. Their greater purity and simplicity of treatment, particularly of the ores in their oxidized zones, caused them to be exploited first and most extensively and to be the dominant factor in the world production of lead at one time. To this type belong, besides many others, the deposits of the Mississippi Valley and Silesia, between them producing 12 per cent of the world's production in 1940.

2. Deposits formed at shallow or intermediate depths genetically associated with igneous rocks, characterized by complex ores and comprising (*a*) vein deposits apparently formed near the surface, (*b*) veins filled under conditions of intermediate temperature and pressure, (*c*) disseminated pyritic replacements of igneous rocks, (*d*) silver-lead replacements in limestone.

Gradations between all these types are found, and many districts have related ore bodies of more than one of these types, sometimes examples of all of them.

With subtype 2*a* are classed certain deposits apparently formed near the surface in genetic connection with igneous rocks and usually occurring as veins, but sometimes as stock works and pipes in volcanic rocks and adjacent sedimentaries, also as replacements in sedimentaries with associated small contact metamorphic masses near igneous contacts. The deposits are usually worked primarily for gold and silver, but small percentages of galena, tetrahedrite, and sphalerite are usually present. The gangue is largely quartz, but adularia, calcite, rhodochrosite, rhodonite, barite, fluorite, and pyrite are often present, and the presence of minerals containing arsenic, antimony, bismuth, tellurium, selenium, and rarely tungsten and molybdenum is characteristic. Successive stages of mineralization are often evident, and secondary enrichment and alteration by descending waters have disguised some deposits.

The ores of the types 2*b* and *c* are usually complex, comprising much of the same minerals of zinc, lead, copper, iron, gold, and silver, and often arsenic, antimony, bismuth, and other metals. In subtype 2*d*, the silver-lead deposits in limestone, zinc is apparently a minor factor, but often when followed to depth, zinc replaces lead as the predominant metal. Many zinc mines are exhausted silver-lead mines.

To subtype 2*a* belong the deposits of the San Juan region and Lake City in Colorado, the Schemnitz deposits in Hungary, the Mapimi and Santa Eulalia deposits in Mexico, and the deposits of Insbach and Freiberg in Germany; to subtype 2*b* belong the

deposits of Coeur d'Alene, Idaho; and to subtype 2*c* belong those of Bawdwin, Burma, and Ridder, Siberia. Subtype 2*d* comprises the deposits of Leadville, Colo., Park City, Utah, and Sierra Mojada, Mexico. The importance of the ores derived from the deposits of the first three subtypes is due largely to smelting practice based on the use of lead as a collector of the precious metals.

3. Deposits in veins originating at high temperature and pressure, in, or associated genetically with, igneous rocks. The ore minerals are blende, galena, pyrite, or pyrrhotite, quartz, calcite, garnet, rhodonite, etc. To this type belong the important deposits at Broken Hill, New South Wales, Australia.

4. Igneous metamorphic deposits containing minerals characteristic of contact metamorphism. The ore minerals are galena and its oxidation products (cerussite and anglesite), blende, smithsonite, calamine, and a gangue of calcite, rhodonite, garnet, py·oxene, hornblende, magnetite, and tremolite. Among the deposits of this type are those of Magdalena, N. M., and the Horn Silver mine, Utah, occurring on or near contacts of limestone with igneous rocks.

Recovery of Lead from Ores.—Metallic lead has been recovered commercially from its ores almost exclusively by smelting in carbon-heated furnaces—either blast or ore hearth. Electric furnaces have been used for complex-ore reduction, but have not become of practical utility, and it would seem that no great promise of development exists in this direction as far as lead is concerned, owing to the high volatility of lead compounds at the operating temperatures obtained in electric-furnace work.

Various processes intended to make available ores of low grade, or complex ores of lead and zinc, have received considerable experimental attention, and a number of commercial plants have gone into operation in the past using hydrometallurgical processes. Among these, the brine-leaching method and the chloride volatilization processes are by far the most important, the former in the field of zinc-lead sulphide and oxide ore, and the latter more particularly in the field of oxidized and semi-oxidized and sulphide ores of copper, lead, zinc, and silver.

The hydrometallurgical treatment of lead ore has been developed to the point where it can compete economically with concentration and blast-furnace smelting on some sulphide ores. The net recovery with concentration and smelting is approximately 85 to 90 per cent; leaching, with or without roasting, will sometimes recover 95 per cent. The mills and smelters already in existence will doubtless continue to operate, but the economic warrant for the erection of smelters may need to be more carefully considered in the future. In general, lead can be produced, at the present time, more cheaply by smelting than by leaching, if the material to be treated contains over 12 per cent of lead. Improvements in concentration have removed some of the former advantages offered by leaching processes, and at the present time their field of application appears to be limited to those low-grade ores which are not amenable to concentration to a point that will make smelting profitable.

Brine-Leaching Methods.—These involve the roasting (sulphating or chloridizing) of the sulphide, solution of the stable lead-silver compounds in acid brines, and the final recovery of the lead by electrolysis or, less frequently, by precipitation on scrap and sponge irons. The free sulphuric acid in the leaching solution limits the solution of the lead; when an average of 8 lb. of metallic lead per ton of mill solution has been precipitated, the same weakened solution can be returned and will dissolve more lead.

An interesting plant, using the Tainton process of brine leaching, went into operation in 1923 in Idaho, the result of extensive experimenting for several years by the Bunker Hill and Sullivan Co. While this plant is not now operating, it is described as an interesting and typical example of lead hydrometallurgy which may find some application in the future. In general, the Tainton process involves the roasting of galena to sulphate in an electrically heated rotary cylinder, at 500°C.;

the removal of soluble sulphates of manganese, magnesium, and other metals by water wash; the solution of lead sulphate in a brine that is saturated with salt and

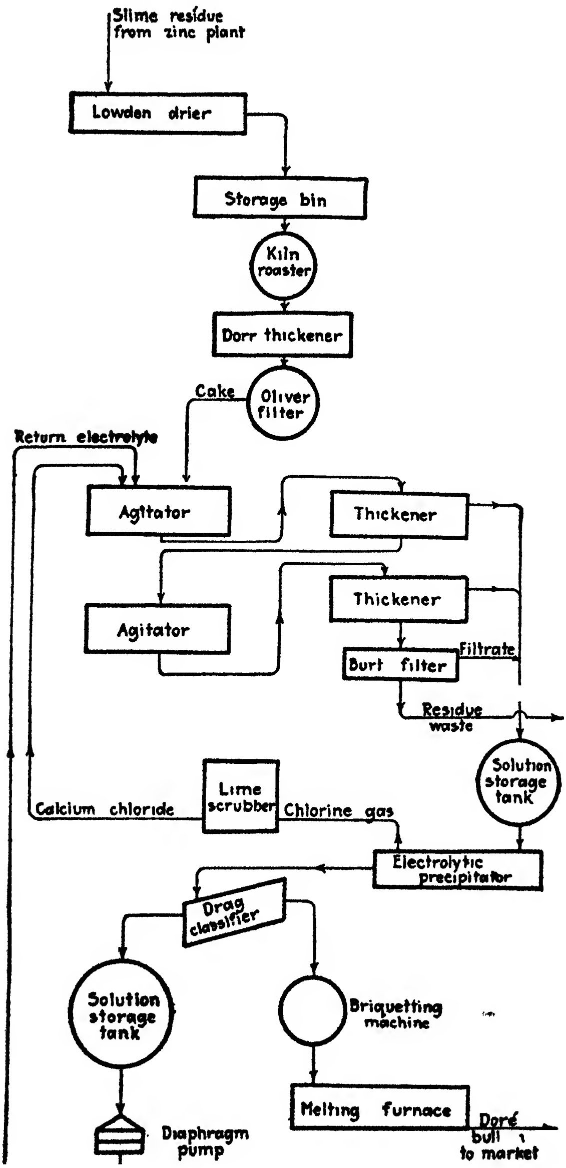


FIG. 1.—Flow sheet, Tainton process.

contains dissolved chlorine from the electrolytic cells; and the precipitation by electrolysis, with high current density and high acid strength, of lead and silver in a cell with rotating sheet-iron cathodes and graphite anodes. The sponge lead recovered

is thrown off the cathode by centrifugal force and floats out of the cell with the brine, or settles at the bottom of the cell, and is pressed into cakes for melting. A 95 per cent extraction of the silver and a 95 to 98 per cent extraction of the lead is possible. The process was developed for application to tailing from lead concentration and from electrolytic zinc production.

The preliminary roasting of the galena is a simple low-temperature sulphating roast (400 to 500°C.), without chloridizing, and the solution of the lead is made possible by the presence of dissolved chlorine in the brine. Ordinarily, and in the majority of other brine-leaching plants, a chloridizing roast is utilized to convert the lead sulphide into soluble chloride form.

Electrolytic-zinc plant tailings, lead sulphate flue dust, lead sulphate sludges from sulphuric acid chambers, oxidized ores of lead containing carbonate or sulphate, concentrating-mill tailing containing lead and silver sulphides, and complex zinc-lead-iron-sulphide ores comprise the products to which brine leaching is adapted.

In similar processes brines, containing dilute hydrochloric acid and also sulphuric acid, are applied in some cases directly to the raw sulphide ores, attacking the galena and leaving the zinc sulphide largely untouched.

The features of the treatment of an ore by such a process are the leaching by agitation of the unroasted ore in a hot brine solution containing a small quantity of hydrochloric acid; filtration and washing with hot weak solution and water; precipitation of the silver by means of lead in some form; precipitation of the lead by cooling the pregnant solution; and reduction of the lead by melting with a mixture of lime and coal dust. The solutions are circulated through spray heaters for re-use. The lead precipitation is based on the fact that a hot liquor at 90°C. will hold 8 to 10 per cent lead, whereas when cooled to 30°C., only 1 per cent will remain in solution.

In another similar process the chloridizing roast is eliminated. When ground very fine, galena will dissolve in a hot saturated and acidulated brine.

Brines carrying ferric chloride are adapted to removing silver, copper, and lead from complex sulphide ores, and have been used in many processes. Ferric brines are more widely used for leaching prepared ore than for attacking raw ores. Chloridized lead can be dissolved in a neutral brine; the silver is so easily precipitated from the solution on such substances as zinc sulphide that almost invariably the brine must also contain small amounts of acid or of ferric chloride or cupric chloride, all of which tend to redissolve any precipitated silver sulphide. A practical method for removing lead and silver from zinc sulphide, developed in Australia, consists of mixing the ore with sufficient zinc chloride to supply 33 per cent excess chlorine over that necessary for combining with the lead, silver, arsenic, antimony, and tin in the ore, and heating to 400 to 500°, out of contact with air. Chlorides of antimony, arsenic, and tin are volatilized, and chlorides of silver and lead remain in the anhydrous mass. These are leached in brine containing hydrochloric acid and ferric chloride.

Chloride Volatilization Processes.—These processes involve the chloridizing roast of the ore and the precipitation of the fume so produced by electrostatic precipitators. Except for the limitation of fume recovery to electrical apparatus, chloride-volatilizing methods are, in general, adapted to a wider range of ore and are less sensitive to trouble than the brine-leaching processes. Metallic-chloride vapors condense as colloidal particles of fume, each surrounded by an adsorbed film of air or gas, which prevents collection by any means other than electrical precipitation. Such particles pass untouched through water and most scrubbing devices, but are efficiently collected in the electrostatic precipitator. Baghouses will make a high recovery, but the corrosive action of the fume rapidly destroys the filtering fabric, and the fact that most such chloride mixtures are hygroscopic causes the precipitated fume to blind the fabric and render the baghouse ineffective.

The application of chlorine in lead metallurgy is important and is discussed elsewhere in the present volume.

Smelting Processes.—The smelting of lead ores is based on three principles: (1) the reduction of lead oxide by carbon or carbon monoxide; (2) the reaction between lead sulphide and lead sulphate or oxide, resulting in a double decomposition with the formation of lead and sulphur dioxide; and (3) the decomposition of lead sulphide by metallic iron. All these three reactions are endothermic, *i.e.*, they require heat supplied extraneously.

1. The first principle is the basis of what is known as the roast-reduction (or blast-furnace) method of smelting, in which lead oxide, lead silicate, or other oxidized compounds must first be prepared from sulphide ore by a roasting operation.

2. The second is what is known as the roast-reaction or air-reduction method—the basis of reverberatory and ore-hearth smelting.

3. The third is the basis of the precipitation method.

All these methods are employed commercially in the United States at the present time, either alone or in combination, the latter being more commonly the case. In practice, the principles are not so distinct as theoretically stated, the reactions fundamental to one process invariably play a certain part in the other processes.

If a lead ore were absolutely pure, there would be no other consideration in the smelting processes than those reactions which relate to lead and its chemical combinations. Practically, lead ores are never pure, the valuable minerals being mixed with a certain proportion of foreign matter, which must be separated by the formation of a slag. In the roast-reaction method of smelting, no slag, properly speaking, need be made, the molten reduced lead being liquated out from the impurities. However, the latter will still retain a high percentage of lead, and in order to effect a high degree of extraction from the ores, they must be subjected to a further smelting process in which a true slag is made. In making a slag, the object is to combine the impurities into a fusible silicate, which, when molten, will be of comparatively low specific gravity, in order that the heavier lead will settle to the bottom of the crucible of the furnace where it may be drawn off separately while the lighter slag will float on top. In addition to the slag and metal, there is formed, usually, a third substance, matte, which is lighter than the metal but heavier than the slag. Under certain circumstances, a fourth substance is formed which is called speiss; this is lighter than the metal but heavier than the matte and, therefore, forms a molten layer between the two. Matte is an artificial sulphide, consisting in lead smelting of the sulphides of iron, lead, and copper. It owes its origin to the incomplete elimination of sulphur from the ore, but is formed intentionally in lead smelting as a means of removing the copper as a separate product. Speiss is formed as the result of the presence of arsenic or antimony in the furnace charge. It usually approaches iron arsenide or antimonide in composition and acts as a collector for other metals such as nickel and cobalt.

The difference between lead smelting in principle and in practice is chiefly due to the incompleteness with which the basic reactions are carried out and the qualifying effect of the impurities that are commonly met with in ores. Thus certain metallic impurities are reduced with the lead, contaminating it and necessitating a subsequent refining process. Other impurities affect the composition of desirable slags. Others affect the running of the furnace in various ways.

If the ores are free from silver, the lead resulting from the smelting process is usually market grade after it has undergone a slight purification by liquating and cooling. To a limited extent the so-called silver-free (Mississippi Valley) lead undergoes treatment by the Parkes desilverizing process, as the amount of total impurities present is considerably reduced, and the price received as a premium for the better grade of lead and the small amount of silver recovered makes the operation profitable.

If the ore is argentiferous, as is the case with practically all districts outside the Mississippi Valley, the silver passes, for the most part, into the lead bullion, and the latter is then desilverized by either the Parkes or the electrolytic process.

The smelting of lead ores is carried on in three types of furnaces: the reverberatory, the ore hearth, and the blast furnace. Of these, the first has become almost obsolete; the ore hearth in recent years has become of considerable importance with a limited class of ores; the blast furnace remains the leading method, since it can treat economically all kinds of ores.

Development of Smelting Processes.—The most primitive form of lead smelting in the United States was practiced with the log and ash furnaces in Missouri prior to 1850. They employed the roast-reaction system of smelting and were applicable only to nonargentiferous galenas of very high grade in lead. They were for the most part displaced about 1840 by the Scotch-hearth furnace. Later, reverberatory furnaces of the Flintshire type went into use, but never extensively nor with such success as to develop a permanent metallurgical practice. The Scotch hearth, however, has survived, and in its modern development is the basis of a highly efficient process in the treatment of certain classes of ore, especially high-grade nonargentiferous galenas.

Neither the Scotch-hearth nor the reverberatory furnace is well adapted to the treatment of argentiferous ore, or to the treatment of ore containing less than 60 per cent lead, while the smelting of carbonate ores alone by either method is not feasible. Neither gives a finished slag or waste product at one operation that can be discarded, and final treatment of their product is usually completed in the blast furnace. For these reasons, by far the major part of the world's lead is produced by smelting in the blast furnace.

In smelting any type of lead ore by any method, the sulphur must be largely removed and the impurities must be combined in a slag, fusible at approximately 1100 to 1200°C., and of specific gravity not to exceed 3.6. In blast-furnace smelting, the slag must be of a composition that will form at the right point in the smelting process, will be thoroughly liquid, in order to ensure a satisfactory separation from the matte, and will require the minimum consumption of fuel, the chief part of which in blast-furnace smelting is always consumed in effecting the formation of the slag.

The sulphur is eliminated in various ways, which may be enumerated as follows:

1. *Roasting.*—Lead ores are usually low in sulphur and therefore are not self-burning in the ordinary roasting furnace. As the decomposition of lead sulphate is effected only by reaction with silica, forming lead silicates, the necessary temperature must be supplied chiefly by the combustion of carbonaceous fuel. The roasting of lead ore may be done in three ways.

a. Ordinary roasting in which the ore is simply desulphurized, at the same time being more or less sintered. Often the ore is partially fused, so that upon withdrawing from the furnace it crusts or may be pounded into cakes.

b. Slag roasting, in which the ore is completely fused.

c. Sintering, in which the sulphides are self-burned and sintered under air blast, either pressure or suction.

The object of roasting is to reduce the sulphur to as low a point as possible, without entailing undue losses in other directions. The sulphur is more completely eliminated by sintering than by ordinary roasting, and more completely by slag roasting than by sintering. At the same time, the loss of lead by volatilization is heavily increased, and in slag roasting it is so high that the process has been abandoned in the United States, save in one or two instances. Ordinary roasting, by which the sulphur is reduced to about 4 per cent, is supplemented by sintering to reduce the sulphur still further and to produce a blast-furnace material of desirable character.

The subject of roasting in general finds detailed treatment in a section of the first volume, "Principles and Processes."

2. *Roast-Reaction.*—Lead sulphide burned partially to sulphate reacts with undecomposed sulphide, setting free metallic lead and sulphur dioxide. This process is effected in the reverberatory smelting furnace, where the charge is first partially roasted and the reaction is then effected under increase of temperature, also in the Scotch hearth wherein the roasting and reacting go on simultaneously. In the modern blast furnace, which is operated under conditions promoting oxidation, roasting and reacting play an important part.

3. *Precipitation.*—Ore is charged raw into the blast furnace, and the lead sulphide is decomposed by iron, precipitating metallic lead, while the sulphur combines with the iron, forming a matte, from which the sulphur is subsequently eliminated by roasting. The quantity of matte to be roasted is apt to be as much as the quantity of ore smelted, but the loss of lead is less than if the ore were roasted originally. There are other drawbacks, however, and this method, which has never had any wide application in the United States, is now employed by itself in only one or two instanc The reaction takes place to some extent in any blast furnace, however, and it, together with the reaction between the sulphide and sulphate described under the previous heading, is largely relied on in modern practice in the blast furnace. Galena of high grade is sometimes charged raw into the blast furnace to save the comparatively high loss of lead which is suffered in ordinary roasting. Precipitation smelting may also be done in the reverberatory furnace, but this method is inefficient and has seldom been practiced either in America or Europe.

After elimination of sulphur by ordinary roasting or by sintering, the ore is ready for smelting in the blast furnace. Naturally oxidized ores may go of course to the blast furnace without any preliminary treatment, save breaking to the proper size.

The universal application of flotation concentration and the high grade and extreme fineness of the concentrate produced have caused sintering to be adopted as a necessary step in blast-furnace smelting. This, in turn, has led to the incorporation of practically all constituents of the blast-furnace charge, including limestone, in the sinter, producing a uniform, self-fluxing charge material, whose characteristics and composition are under close control. The blast-furnace charge commonly consists of 75 to 90 per cent sinter containing 40 to 55 per cent lead, producing a lead content of about 40 per cent in the total charge exclusive of coke.

The Function of the Blast Furnace.—The function of the blast furnace is to reduce the metal and to slag the impurities so that a separation can be made. This separation is effected by the difference in specific gravity of the various products. The specific gravity of liquid (molten) lead is about 10.5, that of matte ordinarily ranges from 4.5 to 5. In order to ensure a satisfactory separation of matte and slag, the specific gravity of the latter should be at least 1.0 lower than the lightest matte. Both the matte and the slag must be thoroughly liquid at the temperature of issue from the furnace. Consequently, the matte must be free from components that make it mushy, such as zinc sulphide, and the slag must be of a composition that is easily fusible at 1100 to 1200°C. The cleanness of the slag, *i.e.*, its freedom from gold, silver, lead, and copper, is dependent chiefly on these physical conditions. The lead content of a good slag should not exceed 1 per cent; the silver content should not exceed 0.2 oz.; the gold content should not be more than a trace. In order to achieve such a result, the specific gravity of the slag should not be more than 3.6, and it should be of approved chemical composition.

In making a slag, the metallurgist is practically limited by the elements that commonly occur in ores, and to cheap fluxes like limestone. The commercial slag is a silicate of two or more bases. The fundamental constituents are silica, iron, and

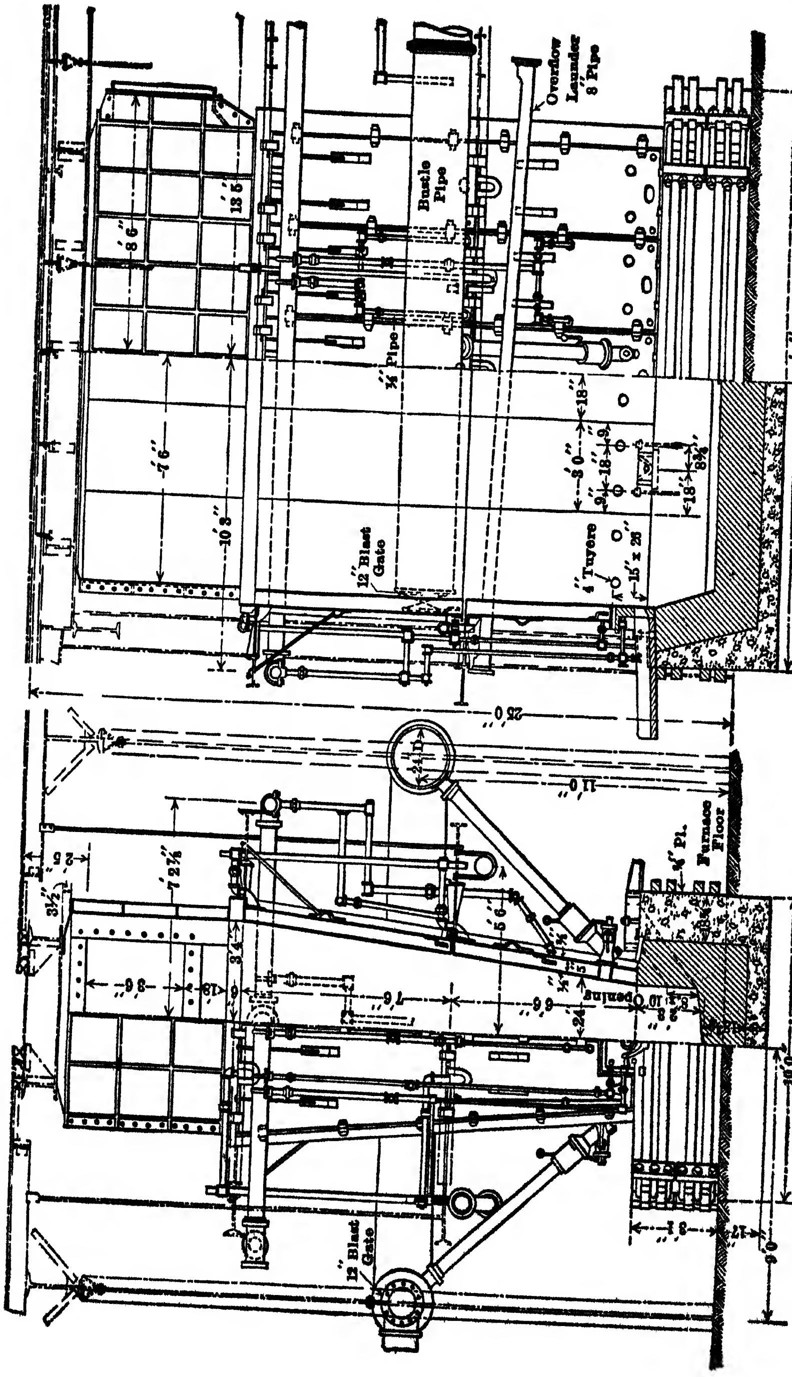


FIG. 2.—Bunker Hill & Sullivan Mining & Smelting Co.'s blast furnace.

lime. The iron may be replaced to some extent by manganese, and the lime to some extent by magnesia, zinc oxide, and barium oxide. These elements ordinarily constitute 90 per cent of the slag. The remainder is chiefly alumina, barium sulphate, and sodium and potassium oxides. In preparing the furnace charge, a mixture of ores and fluxes is made in such proportions as to produce a slag of the desired composition. In lead smelting the permissible range in silica content is rather narrow, varying from 20 to 36 per cent, and ordinarily also the percentages of ferrous oxide and lime range only within narrow limits; the percentages stated nominally as ferrous oxide and lime include their equivalent, respectively, of manganese oxide and magnesia.

The efficiency of the lead-smelting process depends chiefly on (1) the method of sulphur elimination, affecting the cost of the operation, the loss of gold, silver, and lead, and the physical condition of the product delivered to the blast furnace; (2) the design and construction of the blast furnace and its accessories, the method of operation, the physical condition of the material charged, the correct composition of the slag, the character of the bullion produced, and the means of collecting dust and fume; (3) the means for handling products throughout the process.

The better the character of the slag, the faster will be the running of the furnace, *i.e.*, the greater the quantity of charge smelted per square foot of hearth area[1] and the lower the loss of lead and silver in the slag and in the fume. The lower the proportion of very fine material in the charge, the faster will be the running of the furnace and the smaller the percentage of flue dust to be collected and rehandled. The better the character of the bullion, the less irregularity in the operation of the furnace and the less the cost of refining. A detailed consideration of all these governing and largely interdependent factors is possible only in a much larger volume than here presented and will be found in the standard treatises on the subject. It is aimed here to emphasize the general principles of the art and the predominant effect of the make-up of the furnace charge in determining the cost and efficiency of the smelting process. It may be said that the successful development of the silver-lead smelting industry hinges on this matter. As the histories of the various lead-smelting districts are examined, it will appear strikingly how the process was quickly made successful in those which had the advantage of a self-fluxing ore, how it was struggled with in many other districts, and how, as lead smelting became a well understood art, it came to be recognized that an assured and adequate supply of the right classes of ore was the fundamental for the inauguration of a successful business.

Given supplies of silica, iron, and lime, there is no difficulty in producing a slag of any desired composition, but the smelting might be so costly as to be unprofitable. The cost of smelting is properly based on the charge, *i.e.*, all the material except the fuel that is put through the furnace. It is the aim of the metallurgist to have the ore in the charge at the maximum possible percentage, *i.e.*, it is sought to obtain all the necessary fluxing elements in a proper proportion in the ores purchased for smelting, since the time, fuel, and labor required to smelt a pound of flux are the same as for a pound of ore, and for each pound of flux put into the charge there is one pound less of ore. It is, consequently, of the utmost importance to the smelter to be able to secure ores that, upon mixture, will contain the proper proportion of slag-forming substances and will obviate the necessity of making up the proper proportion by the addition of barren fluxes. It is seldom possible to attain the acme of that condition, a small proportion of limestone usually must be added to the charge, and there is always a certain quantity of foul slag, flue dust, roasted matte, and other products that must be resmelted. In the modern American practice of silver-lead smelting, the ore in the charge amounts usually to 80 per cent or more.[2]

[1] The hearth area is the horizontal section of the furnace on the line of the tuyères.

[2] This means 80 per cent or more of the charge, exclusive of the return slag which is used in larger or smaller quantities, often rather large, to facilitate the running of the furnace.

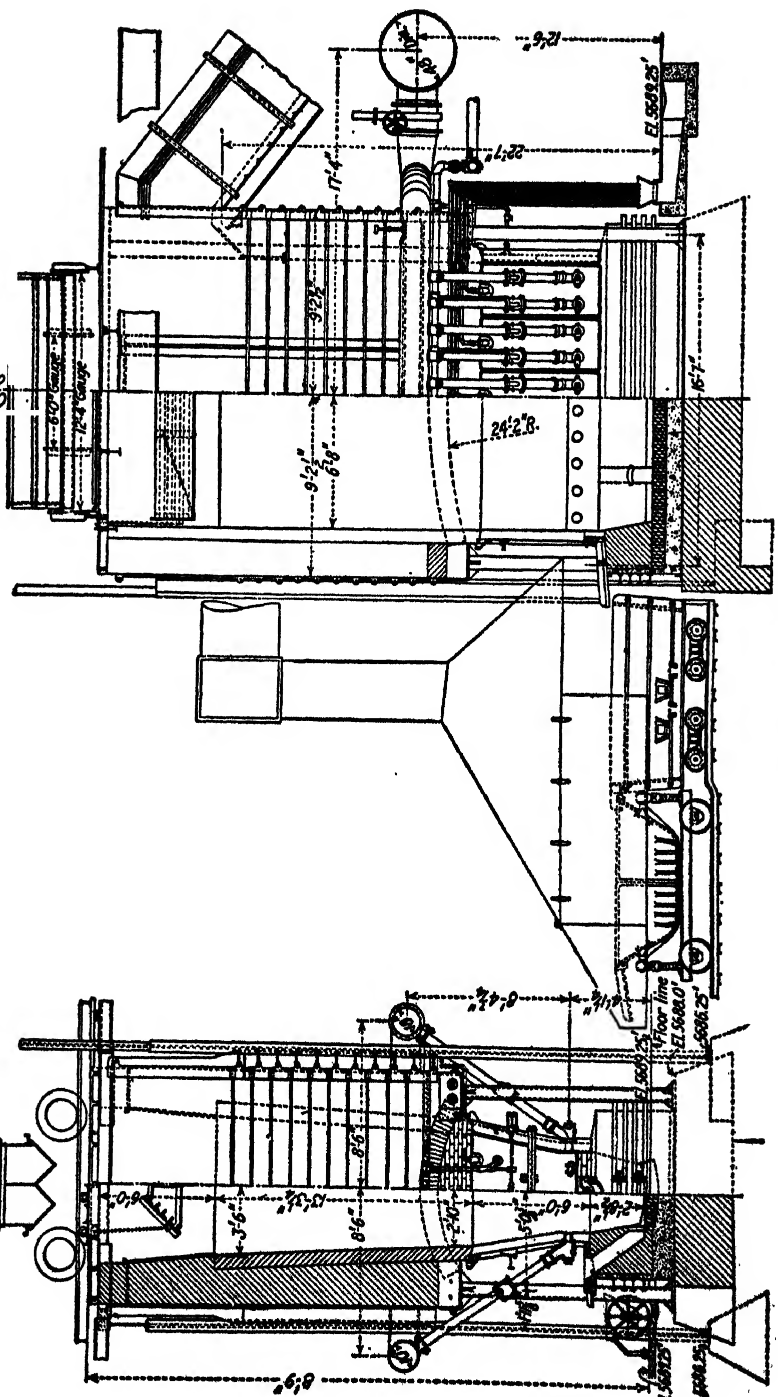


FIG. 3.—Lead blast furnace used at Midvale after 1919.

The practice of the metallurgy of lead has resolved itself at the present time into smelting in the blast furnace for silver-bearing ores and smelting in the Scotch hearth for silver-free ores. In both kinds of smelting the smoke and fume are filtered in baghouses using woolen or asbestos bags. Electrostatic precipitation is well adapted for the collection of fume from all lead-smelting operations and is cheaper in first cost than large baghouse installations. It has been universally adopted for lead-roaster and sinter-plant fume collection, since these gases usually carry elemental sulphur which frequently causes disastrous fires and explosions in baghouses.

With proper fume collection, smelting in the blast furnace yields an over-all recovery in bullion of 95 to 98 per cent of the lead charged. Recoveries of 98 per cent lead are obtained in smelting high-grade galena ores in the Scotch hearth. The two methods of smelting are applied under radically different conditions. In silver-lead smelting in the blast furnace, the prime function of the lead is to act as a collector for the precious metals. The percentage of lead in the blast furnace charge in different smelteries ranges from 10 per cent in blast-smelting crude ores to as high as 50 per cent where the charge is practically all sinter produced from high-grade concentrate. In any case the proportion of slag to ore that is made is much higher than in the treatment of high-grade galena ore in the Scotch hearth, and consequently loss of metal in the slag is higher in the blast furnace. The Scotch-hearth method of smelting has been confined to the treatment of nonargentiferous galena containing 60 per cent of lead or upward. This method of smelting has been improved by the introduction of the Newnam mechanical rabbler, which has reduced labor and improved working conditions, an important item in view of the severity of the latter, especially in hot weather.

The Blast Furnace.—The lead blast furnace has become in recent years practically standardized at modern plants. Materials going into and products coming out of the furnace are handled in almost as many different ways as there are plants in the industry, but in this respect also there is a tendency toward standardization, as hand labor becomes gradually replaced by mechanical equipment. Lead blast furnaces have certain common features, in general the following: rectangular-horizontal section, tapering sides with boshes, straight end, a water-jacketed smelting zone, internal crucible, and the Arents siphon tap for bullion. The circular water-jacketed furnace is used only to smelt at intervals small quantities of intermediary products of a refinery, or for ore smelting in remote localities. The brick shaft common with most ore furnaces has in some plants been replaced in its lower portion by steel water jackets. Furnaces having an entire shaft made up of water jackets are successful, but there is some question of the necessity of the top tier of jackets, and the fuel consumption is said to be higher on such furnaces.

With the increase in size of furnaces and of smelting plants, the transportation of ore flux and fuel by teams and wheelbarrows in the early plants became impossible and reliance on hand labor for manipulation less and less efficient. These early methods have given way to mechanical traction and handling. The necessary apparatus for removing slag from the early small-size furnaces treating mainly oxide ores consisted simply of pots pushed by laborers. As oxide ores were replaced by sulphide, matte handling became a problem in connection with slag handling, solved by extra settling pots which have now given way to large forehearths. As tonnages continued to increase and speiss, dross, furnace accretions, and refractory slags came into the picture in the various smelting centers, compressed air, water, steam, and electric power were brought into play, and mechanical traction, slag granulation, and mechanical furnace manipulation in general are found throughout the industry.

The waste gases in early lead smelting escaped to the atmosphere, carrying damage to crops and man in the immediate vicinity of the plant and resulting in a very con-

siderable loss of metal values. In later periods, settling chambers for catching dust from the smoke stream were provided; these have been supplemented and replaced by baghouses for filtering and by electrostatic apparatus for precipitating the dust and fume. The primitive blowing engines, adequate for blast requirements at first, have been superseded by rotary positive pressure blowers and centrifugal compressors.

General Features of Blast-furnace Design.—The weight of a modern furnace with brick shaft is something over 100 tons. The shaft, the heaviest part, is carried on four cast-iron or steel columns, one at each corner, resting on a concrete foundation extending about 3 ft. beyond the bedplate and supporting columns.

A comparative tabulation of data of design and operation of blast furnaces, based upon a tabulation originally prepared by Hofman,[1] is given in Table 4.

The horizontal section of the furnace is rectangular, the width is most commonly 48 in., ranging from 36 to 63 in. The distance between tuyères is limited owing to the excessive blast pressure that would be required to penetrate to the center of a larger furnace and that would cause excessive volatilization of lead. When furnace charges consisted largely of fine material, the usual distance was 42 in., and this is still a common diameter of small furnaces. With sintered ore and a coarser charge, this dimension increased to 54 and to 63 in., although 44 and 48 in. are the more common figures.

Enlargement of the lead blast furnace has taken the direction, inevitably, of increased lengths rather than width, doubling from the original 60 to 120-in. and later increasing to 160, 192, and 270 in. The limit to which the length of a lead blast furnace can be efficiently increased is an open question. A normal crew can serve a furnace, say, 192 in. long; if this length is increased, additional men are necessary, and the additional tonnage obtained may not be equivalent to the added cost of labor. No great success was at first attained in imitating, on the lead furnace, the great increase in length that brought about such a notable development of the copper blast furnace. Some experiments with furnaces of this type were made as early as 1915 in which the furnace design amounted to practically two normal lead blast furnaces placed back to back with double complements of slag tap and lead well. The balance in a lead blast furnace operating on crude ore is a more delicate one than in a copper furnace, which probably accounted for the failure of many such furnaces to operate successfully. When a lead blast furnace becomes unsatisfactory in operation, it is usually cheaper to blow down the furnace, bar out, and start fresh instead of attempting to nurse it back to normal work. With a copper furnace this is done more readily, and with less loss of metal.

The operation of the lead blast furnace on crude ore and with a small proportion of sinter is delicate owing to the large number of variables that are beyond the control of the furnace operator. However, the increase in percentage of sinter on the charge has resulted in greater uniformity in the condition of the charge in all respects, and the operation has become much more stable.

At Trail, B.C., experiments with increased width and length and smaller tuyère diameter led to the development of a blast-furnace design shown in Fig. 4. This furnace is 270 in. long and 63 in. wide at the tuyères. The bosh increases the width to 84 in. at 5 ft. 8 in. above the tuyères. The furnace has 36 2½-in. tuyères on each side, and these have been shown to give a much better distribution of air than the smaller number of larger tuyères.

This furnace has been very successful in operation and has developed a much higher smelting rate than narrow furnaces of the same length.

The vertical section of a lead blast furnace is marked by an inward "bosh" of the side wall and a contracted tuyère section. This contraction secures a more rapid

[1] HOFMAN, "Metallurgy of Lead," McGraw-Hill Book Company, Inc., 1918.

TABLE 4.—BLAST FURNACES

	National Lead Co., Collinsville, Ill.[2]	Consol. M. & S. Co., Trail, B. C.	U. S. S. R. & M. Co., Midvale, Utah	American Smelting & Refining Co.		
				Selby, Calif.	Arkansas Valley, Colo.	Murray, Utah
Horizontal section at throat (feed floor), inches	156 × 54	84 × 180	95 × 160	60 × 156	84 × 180	93 × 176
Area at throat, square feet	58.5	105	105.55	65	105	113.66
Horizontal section at tuyères, inches	36 × 126	50 × 180	48 × 160	36 × 144	44 × 162	48 × 176
Area at tuyères, square feet	31.5	62.5	53.33	36	49.5	58.66
Ratio throat to hearth area	1.85	1.68	1.98	1.80	2.12	1.94
Height, tuyères to throat (feed floor)	20 ft. 9 in.	17 ft. 3 in.	24 ft. 8 in.	27 ft. 4 in.	19 ft. 6 in.	24 ft. 6 in.
Height, active or working	13 ft. 9 in.	15 ft. 3 in.	16 ft. 0 in.	21 ft. 6 in.	19 ft. 6 in.	16 ft.
Height, tuyères to top of crucible, inches	11	12	13	12	16	15
Water jackets, cast iron or steel	Steel	Steel	Steel	Cast iron	Steel	Steel
Water jackets, number on one side and end	4S 2E	6S 2E	5S 1E	8S 3E	4S 1E	6S 2E
Water jackets, height	4 ft. 6 in.	14 ft.	6 ft. 0 in.	4 ft. 6 in.	5 ft. 0 in.	5 ft. 11 in.
Bosh, height	3 ft. 2 in.	4 ft. 0 in.	4 ft. 1 in.	3 ft. 1½ in.	3 ft. 2 in.	4 ft. 2¾ in.
Bosh, inches per foot, height	3.5	2.25	4.41	3.87	2.21	2.365
Tuyères, number on a side	8	12	10	8	12	10
Tuyères, diameter, inches	4	4	4	3⅛	4	4¼
Tuyère ratio[1]	6.4	4	4.71	3.41	6.09	4.84
Crucible, section at top, inches	116 × 36	180 × 50	160 × 48	144 × 36	162 × 44	160 × 44
Crucible, section at bottom, inches	116 × 36	168 × 50	151 × 30	144 × 36	148 × 24	160 × 44
Crucible, depth, inches	27	24	32.5	27	15 and 27.5	30
Crucible, holds pounds lead	28,000	85,000	....	40,000	40,000	80,000
Lead well, position	Near rear end	60 in. from front	....	Center	31 in. from front	40 in. from front
Lead well, area of channel	8.5 × 8.5 in.	8 × 10 in.	6 × 6 in.	6 × 8 in.	12¼ × 13½ in.	9 × 14 in.
Lead well, area of basin, inches	10 × 10	12 × 14	12 × 12	9 × 9	8 × 13½	9 × 9
Lead well, height of top of basin above top crucible, inches	6	6	10	11	4	6
Forehearth, inside length × width × depth, inches.	63 × 30 × 30	60 diam., 30 deep, circular	108 × 54 × 12	72 × 96 × 27½	82 × 41 × 38	97½ × 43½ × 34
Forehearth, capacity, cubic feet	32.8	30	40	68	73	83.5
Waste slag pots, capacity each, cubic feet	21	(Granulate)	28	25	25	25
Charge (ore and flux), weight, pounds	8000	6000	8000	10,000	6000	8000
Charge, sinter, per cent	0	80	30–65	76	55	52.4
Charge in 24 hr., short tons	248	350	160–300	200	160	263
Charge, tons per square foot hearth area, 24 hr.	7.9[2]	5.6	4.52	5.55	3.2	4.48
Pb, per cent of charge	39.8	35–40	11–18	20–30	11	12.8
Cu, per cent of charge	1.0	Small	0.7–1.0	1.0	0.8	1.02
S, per cent of charge	3.0	1.0	2.5–3.8	3.0	4.0	3.5

TABLE 4.—BLAST FURNACES.—(*Continued*)

	National Lead Co., Collinsville, Ill.[3]	Consol. M. & S. Co., Trail, B. C.	U. S. S. R. & M. Co., Midvale, Utah	American Smelting & Refining Co.		
				Selby, Calif.	Arkansas Valley, Colo.	Murray, Utah
Coke, per cent of charge	10.0	11.5	12.0	12.5	12.0	11.85
Coke, per cent of carbon	82.0	82.5	85.0	82	76.0	81.4
Coke, per cent of ash	14.0	13.0	11.0	13.0	21.5	14.1
Blast, cubic feet per minute	8000	....	5200	6000	....	5000–6000
Blast, ounce pressure	26–32	48	36–42	40	34	35
Cooling water for jackets, gallons per hour	9000	....	Variable	Variable	....	Variable
Men in 8-hr. shift, regular crew	7	6	5	....	3	3
Lead bullion, ounces Ag, Au, per ton	10.0	50.0	80–160	245	169, 3.00	164, 0.41
Speiss, per cent charge	None	Small	....	0.5		
Matte, per cent charge	8.3	None	10.0	10.0	9	7.8
Matte, Pb, per cent	17.0	....	10–18	9–10	12	13.7
Matte, Cu, per cent	7.0	....	6–12	4–8	12	11.7
Matte, Ag, ounces per ton	5.2	....	30–50	20–40	55	44.3
Slag, SiO_2, per cent	29.1	18.0	34.0	25–27	28–32	30–34
Slag, Fe(Mn)O, per cent	33.7	42.0	28.0	40–36	37–31	38–31
Slag, Ca(Mg)O, per cent	16.5	10.5	22.0	17–19	18–21	18–21
Slag, Al_2O_3, per cent	4.0	5.5	3.0	3.5	5.0	3.0
Slag, ZnO, per cent	11.4	19.0	5–9	6.0	7.5	9.0
Slag, Pb, per cent	1.5	1.5	0.6–1.2	0.9	1.0	0.81
Slag, Ag, ounces per ton	0.2	0.15	0.5–0.7	1.0	0.5	0.51
Slag, Cu, per cent	....	....	....	....	....	0.19
Slag, specific gravity	....	....	....	....	....	3.14

[1] Tuyère-ratio = square inch tuyère area: square feet hearth area.
[2] Charge almost exclusively gray slag from ore hearths.
[3] Smelting discontinued, 1935.

TABLE 4.—BLAST FURNACES.—(*Continued*)

	American Smelting & Refining Co.			St. Joseph Lead Co., Herculaneum, Mo.	Sulphide Corporation, Boolaroo,[4] N. S. W.	Bunker Hill & Sullivan M. & C. Co., Kellogg, Idaho	Cons. Mining & Smelting Co. Trail, B. C.
	East Helena, Mont.		Federal, Ill.				
	Fces. 1, 2, 3	Fce. 4					
Horizontal section at throat (feed floor). inches	84 × 192	90 × 170	78 × 144	84 × 192	123 × 201	80 × 180	84 × 270
Area at throat, square feet	112	106	78	112	171.67	100	157.50
Horizontal section at tuyères, inches	42 × 192	48 × 136	42 × 144	50 × 192	60 × 138	48 × 180	63 × 270
Area at tuyères, square feet	56	45	42	67	57.5	60	118.0
Ratio throat to hearth area	2	2.4	1.86	1.66	2.98	1.66	1.33
Height, tuyères to throat (feed floor)	24 ft. 1 in.	24 ft. 1 in.	21 ft. 0 in.	20 ft. 0 in.	29 ft. 8 in.	20 ft. 9 in.	16.3 in.
Height, active or working	15 ft.	Thimble	14 ft. 6 in.	11 ft. 0 in.	24–28 ft.	14 ft. 10 in.	15.3 in.
Height, tuyères to top of crucible, inches	10	12	....	12	16	14	21.5
Water jackets, cast-iron or steel	Steel	Cast iron	Steel	Steel	Cast iron	Steel	Steel
Water jackets, number on one side and end	12S 4E	5S 2E	5S 1E	4S 1E	8S 3E	5S 4E	9S 2E
Water jackets, height	14 ft. (6 ft. 6 in. + 7 ft. 6 in.)	4 ft. 6 in.	5 ft. 9 in.	6 ft. 0 in.	6 ft. 6 in.	14 ft. (6 ft. 6 in. + 7 ft. 6 in.)	14 ft. 9¾ in.
Bosh, height	4 ft. 0 in.	3 ft. 0 in.	4 ft. 8 in.	3 ft. 11 in.	4 ft. 4 in.	14 ft. 0 in.	5 ft. 8 in.
Bosh, inches per foot, height	0.75	0.64	2	3	4.2	1.25	3.7
Tuyères, number on a side	12	8	8	12	7	10	36
Tuyères, diameter, inches	4½	5	4	4.37	3	4	2.5
Tuyère ratio[1]	3.50	4.40	4.79	5.37	1.72	4.19	2.99
Crucible, section at top, inches	192 × 42	136 × 48	42 × 144	48 × 188	54 × 132	45 × 180	63 × 270
Crucible, section at bottom, inches	192 × 42	120 × 48	24 × 144	48 × 168	54 × 132	45 × 168	See Fig. 4
Crucible, depth, inches	36	33	24	29	20	27	See Fig. 4
Crucible, holds pounds lead	90,000	80,000	40,000	50,000	38,500	80,000	66,000
Lead well, position	At second jacket	At second jacket	48 in. from front	1t 5th tuyère	Center side	54 in. from front	45 in. from front
Lead well, area of channel	24 sq. in.	24 sq. in.	4 × 4 in.	8 × 8 in.	4 × 4 in.	8 × 10 in.	
Lead well, area of basin, inches	....	....	4 × 9 in.	10 × 16 in.	4 × 8 in.	8 × 10 in.	
Lead well, height of top of basin above top crucible, inches	9	9	4	6	10	C	

Forehearth, inside length × width × depth, inches.	102 × 42 × 33	102 × 42 × 33	....	98 × 51 × 35	....	Two circular: 6 ft. 2 in. top 3 ft. 8 in. bottom 2 ft. 7 in. deep 5 ft. 6 in. top 3 ft. 6 in. bottom 2 ft. 3 in. deep	Reverb. furnace 10 ft. 6 in. × 18 ft.
Forehearth, capacity, cubic feet	83	83	....	100	1-ton pot	50	40 tons
Waste slag pots, capacity each, cubic feet	28	28	....	23	3	130	Slag to slag-blowing plant
Charge (ore and flux), weight, pounds	9000	9000	5600	12,000	2250	3,000	3250
Charge, sinter, per cent	75	75	70	75–85	75	87	80
Charge in 24 hr., short tons	260	220	214	374	336	425	
Charge, tons per square foot hearth area, 24 hr.	4.7	4.8	5.1	6.30	5.81	7.0	
Pb, per cent of charge	24–28	24–28	35–45	45–50	33	45	40
Cu, per cent of charge	Very small	Very small	0.4	0.4	None		
S, per cent of charge	3.0	3.0	3.8	3.0	2.0	2.0	
Coke, per cent of charge	12.4	12.4	12.9	8.4	12.0	9.5–14	9–11
Coke, per cent of carbon	82.0	82.0	79.0	82.0	83.0	78–82	82
Coke, per cent of ash	15.0	15.0	14.0	7.0	12.0	12–16	15
Blast, cubic feet per minute	7000	5000	6900	7000	7500	6000–7000	
Blast, ounce pressure	32–36	32–36	26	22–36	70	26–32	
Cooling water for jackets, gallons per hour	6000	5100	....	15,000	12,000		
Men in 8-hr. shift, regular crew	3	3					
Lead bullion, ounces Ag, Au, per ton	80	80	Ag, 1.7 Au, 0	Ag 3.8—Au 0	80	Ag 60–100 Au—0.25	45.0
Speiss, per cent charge	None	None	....	None	None	None	
Matte, per cent charge	None	None	5.7	2.5	None	Small	
Matte, Pb, per cent	None	None	22.0	15.1	None		
Matte, Cu, per cent	None	None	12.0	11.1	None		
Matte, Ag, ounces per ton	None	None	2.0	0.75	None		
Slag, SiO_2, per cent	21–25	21–25	28–30	26.8	23	22.0	19.0
Slag, Fe(Mn)O, per cent	45–49	45–39	39–35	36.8	38	35–28	31.1
Slag, Ca(Mg)O, per cent	13–15	13–15	14–16	13.0	17	16–21	9.0
Slag, Al_2O_3, per cent	3.6	3.6	7.5	5.7	5	3.8	5.0
Slag, ZnO, per cent	15.0	15.0	8.5	12.0	12	16.5	23.1
Slag, Pb, per cent	1.0	1.0	1.0	1.6	0.6	1.2	3.5
Slag, Ag, ounces per ton	0.35	0.30	....	Trace	....	0.15–0.40	0.10
Slag, Cu, per cent	....	....	....	....	....	0.12	0.15
Slag, specific gravity	....	....	3.65	3.8	....	3.4	

[1] Tuyère ratio = square inch tuyère area: square feet hearth area.
[2] Charge almost exclusively gray slag from ore hearths.
[3] Smelting discontinued, 1935. [4] Smelting discontinued, 1933.

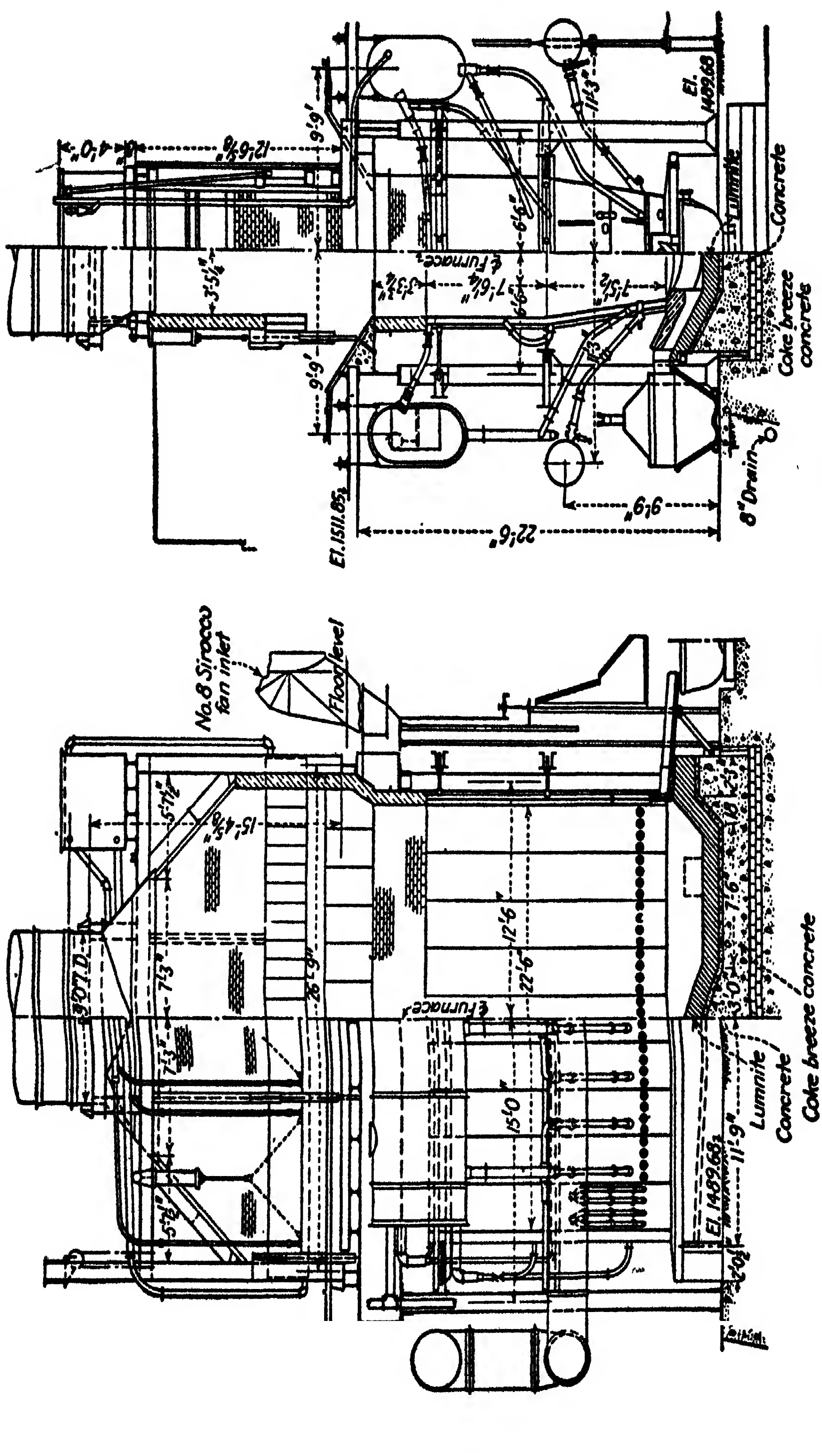


Fig. 4.—Number 10 lead blast furnace at Trail, B. C.

combustion and concentrated intensified heat, resulting in a quicker fusion and more complete decomposition of lead sulphide. When, higher up in the shaft, the width is suddenly increased by the boshes, the gases formed at the tuyères are checked in their upward velocity and more evenly diffused through the descending ore column, giving up their heat to the charge and preparing it for subsequent fusion. In addition the spread of the gases decreases the amount of flue dust carried out of the furnace.

The ends of the furnace are usually without bosh, although some of the earlier plants have end bosh as well as side. Experience generally indicates that the end bosh tends to bring about wall accretions.

Extending upward from the rim of the crucible to the bottom of the brick shaft are the water jackets. These are double-walled steel sections through which water is circulated. They enclose the smelting zone and prevent corrosion of this portion of the shaft by slag. The height to which the shaft is water-jacketed varies in furnace design; however, complete water-jacketing of the entire shaft is generally considered undesirable or unnecessary.

A substantial heat loss, as high at 10 per cent, occurs in the jacket waters. This is reduced and a more uniform operation secured by a closed, or thermosyphon, system for circulation of the cooling water.

The tuyères are circular orifices through the jackets, 2½ to 4½ in. in diameter, usually placed about 13 in. above the rim of the crucible. Through them the blast of air is introduced into the smelting zone. They are placed along the sides and sometimes in the back of the furnace. The side tuyères are spaced 6 to 20 in. apart. The modern furnace takes 5000 to 8000 cu. ft. of air per minute.

The hearth, or crucible, enclosed in brick, concrete, and ironwork, extends from the foundation to the bottom of the jackets. The lines of the crucible are usually a continuation of those of the shaft, and the depth of the crucible ranges from 20 to 36 in., commonly about 30. The crucible, except with very pure bullion, gradually becomes filled with a dross of higher melting point than the bullion, except at the point adjacent to the siphon tap where the temperature is kept higher by the constant withdrawal of bullion. As a result, in most furnaces the crucible is filled with brick or concrete to form a sloping hearth draining to a small wall or sump at the front connecting to the siphon tap.

The Arents siphon lead tap is an opening in the side wall of the crucible. It consists of an inclined square channel about 8 × 12 in. in cross section, leading from the bottom of the crucible side wall, inside, to the top on the outside. At its top, outside the furnace, the channel is enlarged into a bowl-shaped basin, called the lead well. This tap is placed either at the middle of one of the sides or, preferably, a little toward the front of the furnace. When the furnace is running, the crucible should remain full, or nearly full, of lead. The lead in the well will stand higher than the level inside, owing to the pressure of the blast and weight of the charge on the interior surface. The discharge of the lead well is at a level 4 to 10 in. above the top of the crucible. The furnaceman keeps the lead in the well at a height that maintains the lead in the crucible at the top of the hearth, gauging this by experience in tapping. Ordinarily, the furnaceman will close up the lead discharge periodically in order to force the lead in the crucible to rise to a level where some begins to run out with the slag, so that he may know that all speiss, matte, and zinc mush have been cleaned out of the furnace when the furnace slag is tapped "to a blow." With charges running high in lead, 30 to 45 per cent, the lead overflows continuously from the well into a suitable lead kettle at the side of the furnace; with 10 to 15 per cent lead on the charge the well is tapped at intervals.

Handling Ores and Products.—The blast furnace may be considered as the objective point on which turns the entire transportation system and flow sheet of the plant.

The receiving and disposing of raw materials, fluxes, fuel, ores, for the blast furnace and the disposal of its waste, intermediate and primary products, form part of the general arrangement of the whole smelting plant, involving also the sampling and storing of materials, roasting and preparing smelting charges, and the disposition of power, water, and other necessary factors. All this involves an engineering problem of considerable magnitude, detail mention of which is beyond the scope of the present discussion. In sections of the first volume will be found the treatment of sampling, fuel, roasting and sintering, power, fume collection, slag, and other phases of smelting procedure that are more or less common to reduction plants for all metals.

Briefly stated, the products of the lead blast furnace are disposed of as follows:

1. *Lead.*—Crude lead from the lead well is usually transferred to a drossing kettle of 30 to 250 tons capacity where it is freed from impurities held in suspension or solution. This is accomplished by drossing or "poling" (mechanical stirring of the molten lead by means of compressed air or steam) and by the addition of sulphur. The impurities that rise to the surface are slightly oxidized drosses and remain on the surface of the bath, from which they are removed by skimming with a perforated disk or spoon. The agitation exposes new surfaces continually to the air, resulting in the slow oxidizing of copper, sulphur, arsenic, antimony, zinc, and iron which collect on the surface as a dross. When sulphur is added as a drossing reagent, the copper is removed as a sulphide. The kettle of molten lead is allowed to cool to about 480°C. before the dross is removed. After the dross is removed, the lead is air-agitated until the temperature drops to about 360°C., removing constantly the accumulating dross. The temperature is then slightly raised (to about 380°C.) for the taking of "gum-drop" samples (small ladle samples weighing 0.5 assay ton each) and then to about 425°C. for casting the lead. The dross usually goes back to the blast-furnace charge, after being freed by liquation or pressing of much of its occluded lead.

Separate smelting of the dross in a reverberatory furnace for the production of matte and bullion is a recent development. This reduces the production of matte in the blast furnace and eliminates the recirculation of a considerable amount of copper and antimony.

2. *Matte and Slag.*—An imaginary cross section of the crucible of an operating furnace would show the crucible filled with lead, and floating above the lead, speiss, matte, and slag in the order given. The lead leaves the crucible through the siphon tap, which takes off at the bottom, and the other products are tapped through the tap-hole at the front of the furnace, intermittently, into an external receiver or forehearth, in which they separate in accordance with their specific gravity, speiss at the bottom, matte above speiss, and slag above matte. On top of the normal matte there is usually found a zinc mush which separates with difficulty from both slag and matte.

This zinc mush, inside the furnace, and outside as well, is the bane of lead furnace-men and metallurgists; it is the root of furnace troubles which may vary in intensity from merely unsatisfactory assays (metal losses) to the entire loss of the furnace through freezing or slagging (mushing) of tuyères. More than any other single factor, the solution of the zinc-mush difficulty is to eliminate the possibility of its formation, primarily, by the exclusion of zinc-bearing materials from the charge, or if this is impracticable, by ensuring the dead roasting of all zinc sulphide of the charge. Zinc combined with sulphur spells trouble; zinc combined with oxygen is handled and slagged with comparative ease. Zinc entering the blast-furnace slag is no longer a total loss, but in modern practice is recovered with a considerable portion of the lead by further treatment of the slag. Improvements in selective concentration and in sintering practice have been the largest factors in meeting the zinc situation. There are two other points in the lead blast-furnace manipulation of zinky charges that, although not so generally known, are recognized at certain plants as of almost equal

importance in combating zinc troubles. At Namtu, Burma, where slag zinc runs up to 30 per cent ZnO, it has become recognized that zinc troubles are not always sulphur troubles.

Some of the most troublesome work on record at the Namtu furnaces occurred when the physical condition of the sinter was quite up to the average, with sulphur only 2 per cent, furnace clean, coke good, and when the analysis of the resultant slag was in line with their best type. Trouble appeared because, although the zinc and iron were in the charge in the correct proportion, they were not there in the correct condition. No trouble is encountered when the iron necessary to satisfy the slag demands of the zinc exists in the charge in intimate association with the zinc and when, also, a comparatively small amount of slag material has to be made to carry the zinc in the concentrator; it is a really troublesome matter when the iron requisite for a heavy zinc charge has to be supplied almost entirely, as at Namtu, by the addition of limonite and, to obtain satisfactory combination, a considerable heat reaction is required. At Namtu, it is also to be noted that a slag fall of 2 to 1 is obtained by the amount of slag that has to be formed to carry the zinc, even when this slag contains 30 per cent ZnO.

At Cockle Creek, New South Wales, control of zinc troubles had been secured, prior to the shutting down of this plant of the Sulphide Corp., by smelting methods that were almost unique in lead blast-furnace practice. A combination of high ore columns (26 to 28 ft.) and high blast pressure (approximately 70 to 75 oz.) maintained an intensity of temperature at the smelting zone and a drive of the furnace that resulted in remarkable freedom from zinc accretions and trouble and gave slag carrying well under 1 per cent lead, with no unusual losses in any direction.

Where matte is made in appreciable quantities, large movable forehearths (about 8 × 4 × 4 ft.) receive the stream of slag and matte tapped from the furnace. The matte and speiss produced are trapped and accumulate in the forehearth, while the slag overflows from the top. At intervals, the matte and speiss are tapped through the side of the forehearth. The waste slag pots are removed by a locomotive and the slag disposed of either by pouring over the dump or into a granulating apparatus. In most large smelteries, this molten slag is now transferred to a slag-blowing furnace where the zinc and lead are largely removed as a fume and collected.

Formerly, all shells and crusts from waste slag pots were brought back to the blast furnace for resmelting, because of enrichment of lead and silver in the shell, fluxing requirements, and beneficial effect on the blast-furnace charge, but the practice of recent years tends to discontinue the resmelting of slag shells, substituting the resmelting of forehearth bottoms. Two forehearths in series are frequently used, with consequent throwing away of the entire contents of the slag pots. In a few instances the slag-matte mixture tapped from the blast furnace is transferred to a small reverberatory settling furnace from which matte and slag are intermittently removed. In some instances, granulating places the slag in a form that can be easily disposed of by sluicing away, when sufficient water is available; it also provides a form of slag well adapted for mixing with the sinter charge. Most large smelteries in which a considerable amount of zinc enters the blast-furnace charge now re-treat the blast-furnace slags by blowing. A large part of the zinc and lead contained in the slag is removed as oxides and is collected in the form of dust or fume in baghouses and cooling flues. A considerable tonnage of slag reclaimed from old dumps is being re-treated for recovery of its zinc and lead content by this method. The blowing furnace resembles a blast furnace in general construction. It has a rectangular water-jacketed shaft with tuyères along each side a short distance above the bottom. Molten slag is poured in at the top of the shaft to maintain a depth of molten material above the tuyère line. Pulverized coal is blown in with compressed air through the

tuyères into the bath of molten slag, the zinc and lead oxides in the slag are reduced and the metal vapors are reoxidized in a combustion chamber above the surface of the slag and are carried away through flues to the collecting equipment. The molten slag after blowing is tapped out of the furnace and disposed of.

The matte contains silver, gold, lead, and copper and must all be re-treated. Three methods of re-treatment are in common use: (1) The matte is crushed or granulated, mixed with the roaster or sinter feed, and desulphurized before being returned to the blast furnace. (2) The matte is resmelted as a separate operation of "matte smelting" to lower the lead content by replacement with iron and to concentrate the copper content to a point where the matte may be sold to a copper smelter. (3) The matte is treated in a standard basic lined copper converter, with or without the addition of siliceous fluxes. Air is forced through the molten matte at a temperature of 1100° to 1200°C., oxidizing the S, Fe, and Pb. The iron is slagged as silicate by the fluxes, or as molten Fe_3O_4 if no fluxes are added. The lead is slagged or driven off with the sulphur as a basic lead-sulphate fume. The Cu, Ag, and Au remain and are combined with copper matte and reduced to metal by a continuation of the converting operation. The lead-bearing slag and lead fume produced in the converting operation are re-treated in the blast furnace.

3. *Fume and Dust.*—Hoods are placed at all points around a blast furnace where fumes arise, the pipes from all hoods lead to a main flue and exhaust fan which deliver to a baghouse or electrostatic precipitator. The gases and dust issuing from the top of the furnace, combining with the fumes from the tapping floor, travel through flues and chambers in which they drop most of their dust, and then to special condensation or filtering apparatus. The methods for recovery of flue dust and fume at lead smelteries and refineries may be classed as dry, wet, and electrostatic. In Chapter XII of the first volume the subject of dust treatment is discussed in greater detail.

Chemistry of the Lead Blast Furnace.—The charge—ore, flux, and coke—fed at the top of the furnace is subjected as it descends through the shaft, in about 8 hr., at gradually increasing temperatures, to chemical reactions and physical changes that transform it into lead bullion, speiss, matte, slag, and gases. The two processes principally involved are reduction and precipitation, and incidentally sulphurization, at temperatures ranging from 1100 to 1200°C. at the tuyère level to 150°C. at the throat.

The principal reducing agents are C and CO. The carbon, supplied by the coke (normally 8.5 to 13 per cent of charge), acts on metallic oxides as soon as the temperature rises to a point where its affinity for oxygen is greater than that of the metal that is combined with the oxygen; this action begins at about 400°C. The products of oxidation are CO_2 and CO. The former results if the metallic oxide is easy of reduction, say below 1000°C., the latter if the oxide is difficult of reduction, perhaps above 1000°C. The reducing action of CO, which begins at about 200°C., increases with temperatures up to about 1000°C., beyond which point it falls off rapidly.

The principal agent of precipitation is iron. Other metals act as precipitants also, in conformity with their affinities for sulphur. Each metal will displace from sulphides other metals whose affinity for sulphur is weaker. According to Fournet such replacement is in the following order:

Cu—Fe—(Co—Ni)—Sn—Zn—Pb—Ag—Hg—Au—As—Sb

The more recent work of Schutz places the series in a slightly different order, as follows:

Mn—Cu—Ni—Fe—Sn—Zn—Ag

Precipitation, or decomposition of sulphide by metal, begins at about 900°C. and is at a maximum at tuyère level, where the furnace temperature is around 1200°C.

The precipitation reaction is reversible, however, and the complete decomposition of the metallic sulphides by iron is thus counteracted to some extent.

Descending Ore Charge.—In considering the changes in the descending ore charge, it is convenient to distinguish four zones: the zone for preparatory heating, 100 to 400°C.; the upper zone of reduction, 400 to 700°; the lower zone of reduction, 700 to 900°; and the zone of fusion, 900 to 1200°. There is no sharp line of demarcation between the zones, one passing over into the other; the reactions beginning in one zone may be finished only in the next or perhaps even the second lower down. The process of heat interception is continuous from the tuyères to the throat, or from 1200 to 100°C.

1. *Zone of Preparatory Heating* (100 *to* 400°C.).—The charge fed into the furnace first gives up its hygroscopic water, then that which is chemically combined. Clayey material, limonites, and some other hydrates give up only part of this water at 400°C. The evaporation of water absorbs heat and thus assists in keeping the top of the furnace cool.

2. *Upper Zone of Reduction* (400 *to* 700°C.).—The decomposition of hydrates continues, the dissociation of carbonates and of some sulphates begins. The reducing effect of CO, which theoretically begins at 200°C., becomes noticeable only at about 400°, and increases with rise of temperature up to about 900°. It will, therefore, be an active agent in reducing PbO completely to Pb, and $PbSO_4$ partly to PbS; it will also start the reduction of Fe_2O_3. The C of the coke, which begins to act reducingly at about 400°C. and increases as the temperature rises, will change PbO completely into Pb, and $PbSO_4$ partly into PbS; it will assist CO in its reduction of Fe_2O_3, and will transform CO_2 of the gas current into CO. There will further take place reactions of $PbSO_4$ and PbO and PbS, setting free Pb and SO_2.

3. *Lower Zone of Reduction* (700 *to* 900°C.).—The reactions started in the preceding zone continue and are in part completed; the effect of C becomes more marked than that of CO. The $CaSO_4$ in sintered ore as well as $BaSO_4$ in raw ore are more or less reduced to CaS and BaS to be dissolved later on mainly by the slag. The dissociation of carbonates is about completed, $CaCO_3$ at 910°. The union of SiO_2 with unreduced PbO and $PbSO_4$ begins, as does the decomposition of PbS, $PbAs_x$, and $PbSb_y$ by Fe; sulphurization of Cu begins at about the same temperature. Matte of eutectic composition begins to soften. Everything is prepared to be liquefied and to bring to completion the chemical processes.

4. *Zone of Fusion* (900 *to* 1200°C.).—The reductions of oxides, including ZnO, and decompositions of sulphides are completed; ascending Zn vapor is oxidized and sulphurized. Lead reduced in the upper parts of the furnace trickles through the charge, picking up Ag on its way, and acting possibly upon lead arsenate and antimonate; it joins the Pb set free lower down from PbS, $PbAs_x$, $PbSb_y$ and continues to take up Ag. The sulphides of eutectic composition, which softened higher up, become liquid and dissolve other sulphides to form matte with a melting point lying below that of slag formation. The slag components SiO_2, FeO, and CaO form a slag of lowest formation temperature and this, trickling downward, dissolves the remaining SiO_2, FeO, CaO, as well as other bases, such as Al_2O_3 and ZnO. Scorified PbO is set free and reduced by C to Pb. The three main products—lead, matte, and slag—settle in layers according to their specific gravities; lead passing downward through slag and matte robs them of some precious metal; matte in a similar way removes Pb, Cu, and Ag from the slag; at the contact planes of the products, interchange of components takes place to a moderate degree with a tendency to collect sulphide in matte and metal in lead. The lead passes off through the lead well; speiss, matte, and slag are tapped into the forehearth, from which slag overflows into a waste-slag pot or granulating apparatus, and speiss and matte are tapped periodically into suitable receivers.

Mechanical Feeding of Charge.—The metallurgical and practical success of a blast-furnace operation depend as much on a proper physical condition of charge and its accurate distribution in the furnace shaft, as on the actual constituents of the charge and their accurate calculation by the metallurgist in control. One of the greatest steps in the advance of lead blast-furnace work occurred when the old hand-feeding methods were replaced by mechanical feeding, about 1900, along lines developed by A. S. Dwight in Montana. This mechanical-feeding system and the general adoption of sintered products in the ore charge constitute the major improvements in the smelting of lead that have been developed in many years. Tonnages and metallurgical recoveries were enormously benefited by these steps, which almost revolutionized art.

Charge components, made up of ore, flux, fuel, and secondary products, va greatly in size. In an ideal assortment of sizes, about one-third of the charge wou

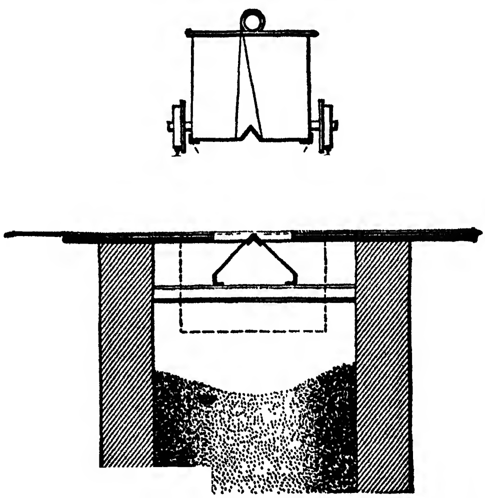


FIG. 5.—East Helena feeder with Dwight spreader.

be in pieces 5 to 2 in. in diameter, one-third 2 to ½ in., and the remaining third ½ in. down.

A coarse charge is preferable to a fine one, as the ascent of gases is more uniform; if too coarse, however, the gases pass up and away too quickly and do not get in their proper work on the descending charge. A fine charge obstructs the flow of gases to too great an extent, and the gases tend to break through at various points in the form of blowholes, which upset the chemistry and operation of the furnace completely and cause loss by carrying off dust and fume. In furnace work there is always the danger of fines trickling through the coarser parts of the charge and reaching the smelting zone in a crude state, chilling the furnace, and even clogging the tuyères. In modern smelting, with charges made up largely of sintered materials, the fines have been reduced to such an extent that they seldom cause trouble.

In general, the coarser parts of the charge must be placed toward the center of the shaft, and the finer material toward the side walls. The ascending gases have a tendency to hug the sides of the shaft, and their passage must be adjusted by charge distribution, so that the gas current will ascend evenly and uniformly over the whole area of the smelting column. The method of mechanical feeding developed at East Helena by Dwight in 1900 is at present in use at the majority of plants, in more or less modified forms. The principle used is shown in Fig. 5.

The contents of the charge car (4 tons) drop onto an A-shaped spreader which throws everything toward the sides of the furnace shaft where the bulk of the fines remain, while the coarser parts roll down the inclined surface or trough of the descending charge and gather along the center axis. To prevent carrying this segregation of coarse and fines too far, a modification of the Dwight spreader was adopted by W. W. Norton at Murray, Utah, in which the A-shaped spreader, instead of being a solid casting, was made up of several parts separated by open spaces, or slots, as shown in Fig. 6. The charge, on dropping onto this spreader, is not all deflected toward the side walls, but a portion falls directly through the slots and lands in the center of the furnace. A satisfactory distribution of charge results, much fine with some coarse along the sides, and much coarse with some fine along the center.

With charges in recent years made up so largely of sintered product, and the consequent greater smelting speed of the furnace, there is less danger of the heat

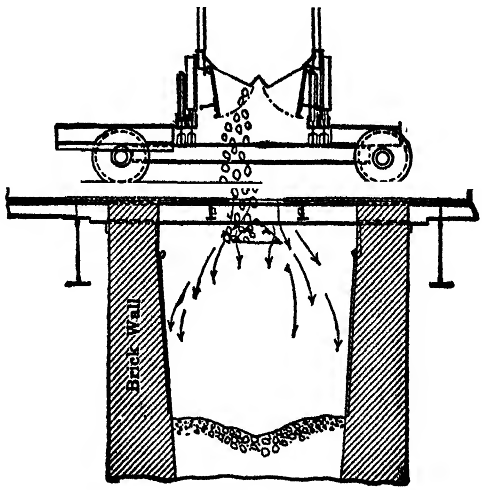


FIG. 6.—Dwight-Norton spreader.

creeping up in the furnace, and there is now a tendency to try to distribute coarse and fine more evenly through the furnace.

Smelting Lead Ores in the Reverberatory Furnace.—Until within comparatively recent years the smelting of sulphide lead ores in the reverberatory furnace was very common, especially in England, Belgium, and Austria. Since sintering has come into general use, however, reverberatory work has become nearly obsolete. In the United States in 1877 there were 56 reverberatory furnaces in operation in Missouri, in 1940 only 2.

The process involved was the roast-reaction, or air-reduction, process, based on the reactions between PbS, PbO, and $PbSO_4$ at temperatures below 1000°C., which set free Pb and SO_2. The precipitation process, based on the decomposition of PbS by Fe, was formerly in operation with raw lead ores in France and in the United States at one plant at Chicago, also with roasted ores in Cornwall. The precipitation process, as a separate procedure, has been given up because of high cost and heavy loss of metal.

The roast-reaction process in the reverberatory furnace involves two operations, oxidation and reduction, one following the other closely, and both being repeated several times. The finely crushed ore, spread in a layer 4 in. deep on the hearth, is heated gradually to a full red (500 to 600°C.). The roasting is carried on in such a

way that only a part of the PbS is converted into PbO and $PbSO_4$, the rest remaining undecomposed. The second step of the operation is that of raising the temperature to about 800°C. so that the oxygen compounds may react on undecomposed sulphide. The resulting metallic lead runs down the inclined hearth and collects in a basin, the SO_2 escapes into the flue, and the residue remains on the hearth. The temperature must remain low during this reduction period, so that the charge will not melt, but will remain in a pasty condition. The reactions are imperfect if the ore is melted.

It was found to be impossible to roast a large amount of lead ore uniformly in one operation in this manner. The first reaction that takes place on raising the temperature will not extract all the lead. The residue will contain rich PbS, with some lead oxide, lead sulphate, and lead silicate. The temperature is lowered, air admitted, and a second roasting takes place, followed by a second reduction. This cycle is repeated several times before the bulk of the lead is extracted. With each successive reduction, the temperature must be raised slightly, as the amount of lead diminishes. To counteract the melting of the charge, slaked lime is added. Toward the end of the process, there will not be enough PbS left to react on the PbO and $PbSO_4$, and to reduce these, coal is mixed in. Each successive operation is of shorter duration than the preceding one, and the metallic lead obtained is each time a little less rich in silver.

The products of reverberatory smelting are as follows:

1. *Lead.* If clean enough this can be rendered fit for market by simply liquating and poling; if it carries silver, arsenic, antimony, or copper, refining must be resorted to.

2. *Gray Slag.* This is a more or less matted mixture of lead (PbS, PbO, $PbSO_4$, $PbSiO_3$), gangue, cinders, and lime, with some silver. It is crushed and smelted in the blast furnace.

3. *Flue Dust.* This consists mainly of oxidized compounds and is worked in with subsequent charges, shortening the time required for roasting. If very impure, it is smelted in the blast furnace, with the gray slag.

4. *Hearth Bottom.* This consists of hearth material impregnated with metal. It is worked up in the same manner as the residues.

Limitations of Roast-reaction Process.—To be suited for the reverberatory furnace, an ore must be a rich galena, or a mixture of galena and carbonate, that does not contain less than 60 per cent Pb, 70 per cent being preferable. It may not contain more than 4 or 5 per cent SiO_2, and its content of zinc blende, pyrite, chalcopyrite, calcite, and barite must be low. The process takes heavy fuel and much skilled labor.

Classification of Reverberatory Methods.—Reverberatory procedure varies widely in different countries, three distinct methods of reverberatory work being recognized. Carinthian, English, and Silesian. Some of the principal plants work toward the object of extracting as much lead as possible in the reverberatory (Carinthian and English), while others supplement the reverberatory by the blast furnace, taking out only a major portion of the lead in the former. The rich residue from the reverberatory, smelted in the blast furnace, permits a higher total extraction (Silesian). Some establishments roast the ore slowly at a low temperature, thereby obtaining a maximum recovery of lead (Carinthian and Silesian), while others conduct a hurried high-temperature roasting, aiming to save time and labor at the expense of metal (English). Reverberatory furnaces vary in form and size also.

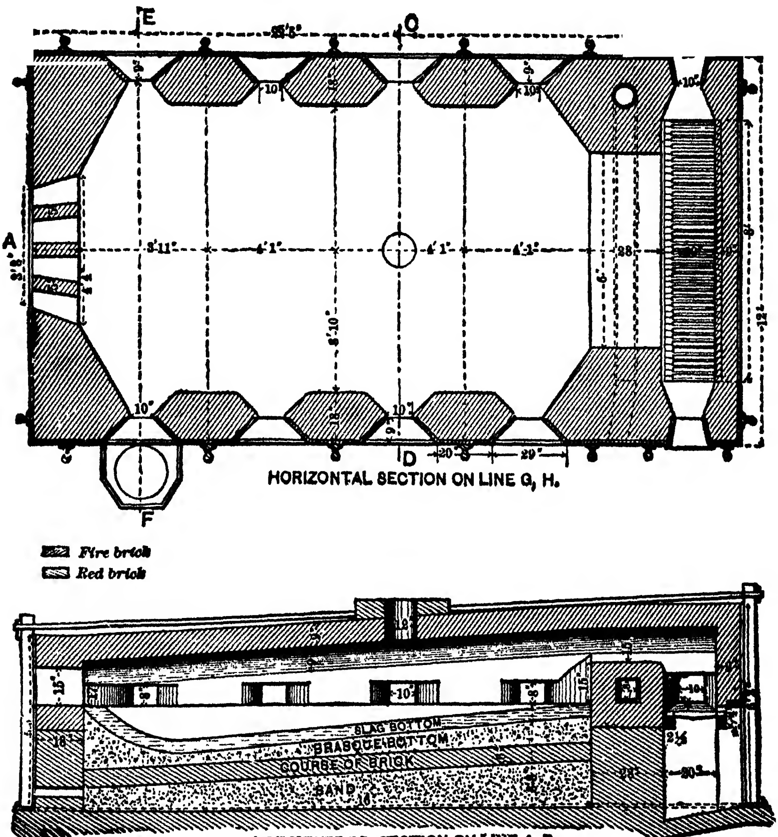
The Carinthian method is distinguished by the smallness of the charge, slow roasting, low temperature of all operations, and the extraction of all the lead in the reverberatory. The hearth is inclined toward the flue and the lead collected outside the furnace.

The English method is marked by a large charge, quick roast, high temperature throughout, and extraction of all the lead in the reverberatory. The hearth slopes

toward the middle of one of the sides, and the lead collects inside the furnace, being tapped at intervals into an outside kettle.

The Silesian method is characterized by a large charge, slow roasting, and a low temperature, the lead being only partly recovered in the reverberatory, which is supplemented by the blast furnace. The hearth is inclined toward the flue, beneath which the lead is collected and tapped at intervals into an outside kettle.

The Silesian furnace (Tarnowitz) is shown in Figs. 7 to 9.



FIGS. 7–8.—Silesian reverberatory furnace.

Smelting Lead Ores in the Ore Hearth.—The ore hearth has come back into an important position in the lead industry during the present century. It is an ancient method, with operating principles that may be said to be intermediate between a reverberatory and a blast furnace. At first the only method for working low-silica high-grade galena ores, it passed into disuse and became largely replaced by the reverberatory furnace, but the reverberatory has given way, with the advent of the baghouse and Cottrell electrostatic processes for the collection of fume and dust, and the ore hearth, in modern mechanical form, has taken a new lease of life. In 1914, there were in operation in Missouri alone 75 ore hearths (hand operated) with an annual capacity of 230,000 tons of galena concentrate; by 1923, the Newnam mechanical ore hearth had replaced all the hand hearths on the American continent;

about fifty of these furnaces were in operation in 1941 with a capacity of 500,000 tons annually.

Plants have also been erected, and are at present in operation, in Canada, England, Spain, and South America, treating not less than 60,000 tons.

An ore hearth is, essentially, a low fireplace surrounded by three walls, with one or more tuyères at the back. It is invariably made of cast iron. In the front there is a cast-iron "work plate," with a groove to carry off the reduced lead into a kettle. There is usually a partial front wall composed of a thick bar of iron, but often the front is simply a dam formed of ashes and powdered galena which is impervious to melted lead. The sides and back must be of iron in order to admit of chipping off

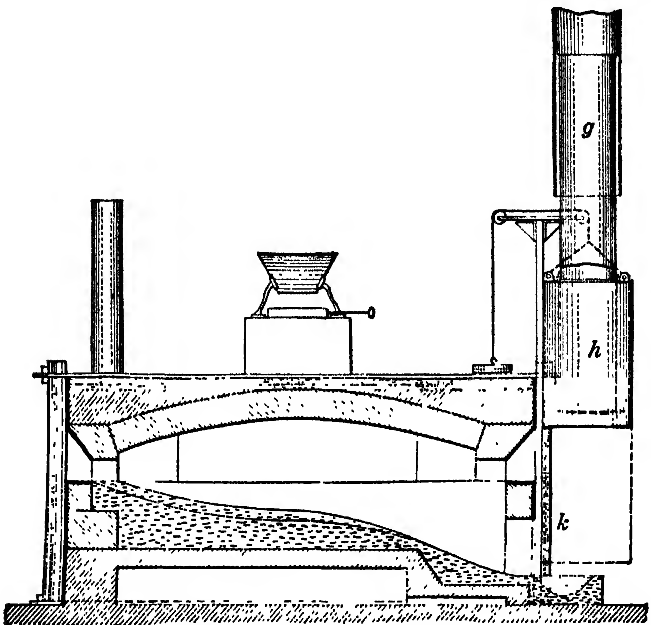


FIG. 9.—Silesian reverberatory furnace.

the half-fused masses of slag that constantly adhere to them; they may be cooled simply by radiation from large heavy castings (Scotch hearth), by a current of air (Rossie hearth), by a water box (American water-back hearth), or by both air and water boxes combined (Moffet-Jumbo hearth). These differences may conveniently be taken as indicating the four distinct modifications of the hearth process, though the manipulation is much the same in all. The Newnam mechanical hearth, water-cooled, is, of course, a fifth type.

The process carried on in the ore hearth is mainly the roast-reaction process, resembling that of the reverberatory furnace, but differing in the respect that roasting and reduction go on simultaneously and that there is considerable direct reduction of lead oxide to metal by the carbon of the fuel. The charge—ore and fuel—floats on a bath of molten lead; the PbO and $PbSO_4$ react on undecomposed PbS; some PbO is reduced by C; and the metallic lead trickles through the charge to the bottom, overflowing into an outside kettle.

The character of the ore to which the hearth process is adapted is determined by much the same limitations as for the reverberatory furnace. These limitations,

TABLE 5.—EXAMPLES OF SMELTING IN REVERBERATORY FURNACES

Items	Carinthian method					English method			Silesian method	
									Tarnowitz, Silesia	
	Raibl, Carinthia	Engis, Belgium	Granby, Missouri	South-west Missouri	South-east Missouri	Holywell, Flintshire	Stiper-stones, Shropshire	Desloge, Missouri	Old furnace	New furnace
The furnace										
Hearth, length	11'	6' 6¾"	9'	[*] 9	10'	12'	9' 9"	16'	11' 9"	16'
Hearth, width at bridge	5'	4' 3⅛"	3' 2"	3'	2' 6"	3' 6"	4'	....	....	6'
Hearth, width at middle	5'	4' 4¼"	3' 2"	3'	4'	9' 6"	9' 6"	11'	10' 10"	8' 10"
Hearth, width at flue	1'	2' 3½"	3' 2"	3'	2'	4'	3' 3"	....		4' 4"
Hearth, thickness of bed	6"	1' 5¾"–2' 8¾"	6"	6"	....	2"–10"–26"	4"–18"–30"	8"		4"
Hearth, life of bed, weeks	4–5	6	....	....	....	....	....	....		13
Hearth, inclination to flue or side	21" F.	17" F.	18" F.	–F.	–F.	29" S.	24" S.	....		27½" F.
Grate, length	7'	3' 7¼"	5' 6"	6' 6"	3'	4' 6"	4' 6"	8'	Similar to new furnace.	8'
Grate, width	1' 3⅜"	1' 6"	2' 6"	2' 6"	2'	2' 6"	2' 6"	1' 3"		1' 8"
Grate, depth below top of bridge	1' 2⅜"	3' 7¼"	....	6"	....	2' 9"	1' 4"	....		3'
Bridge, width	5⅝"	1' 3¾"	8"–30"	....	21"	24"	24"	....		28"
Bridge, length	3' 7¼"	3' 11¼"	30"	30"	24"	42"	48"	....		72"
Bridge, height above hearth	4–5"	none	....	6"	....	12"	12"	....		15"
Roof, height above bridge	9"	8⅝"	14"	....	6"–8"	9"	19"[1]	....		12"
Roof, height above hearth at flue	12"	2' ⅜"	14"	....	6"–8"	16"	20"	....		17"
Flue (leading to chimney), size	1'×1' 3¾"	8¾"×2' 3½"	8"×12"	....	12" diam.	12"×10" 10"×10"	12"×12" 11"×12"	2(16"×18")		4(15"×20")
Chimney, inside size	1'8"×1'8"	1' 3"×1'	....	....	12" diam.	3'×3' 6"	....	42" diam.		....
Chimney, height	20'	....	....	20'	15'	....	....	55'		....
Grate area, ratio to hearth area	1:6	1:5.25	1:2.0	1:1.66	1:5.4	1:8	1:6.6	1:7.3		1:10
Grate area, ratio to section of chimney	1:0.14	1:0.47	....	....	1:0.13	1:0.93	....	1:0.40		....

[*] Kemp, *School of Mines Quarterly*, 1887–88, IX, p. 212.

[1] Height of roof above grate, 38".

TABLE 5.—EXAMPLES OF SMELTING IN REVERBERATORY FURNACES.—(*Continued*)

Items	Carinthian method					English method			Silesian Method	
									Tarnowitz, Silesia	
	Raibl, Carinthia	Engis, Belgium	Granby, Missouri	South-west Missouri	South-east Missouri	Holywell, Flintshire	Stiper-stones, Shropshire	Desloge, Missouri	Old furnace	New furnace
Work done										
Charge, weight in pounds	370-430	1,375	1,500	1,500	...	2,350	2,350	3,325	4,400	8,250
Charge, assay, per cent. lead	70	76	...	...	...	75–80	77.5	70	70-74	...
Charge, thickness on hearth	1⅛"–1½"	about 3"	...	...	...	1⅝"?	3⅞"–4⅛"	...	3"–4"	3"–4"
Operation, length in hours	10–12	12	12	9–11	...	6	7	8	12	12
Men, number in 24 hr.	1.5	4	2	2	...	6	4	6	4	6
Gray slag, amount in pounds	95	275	...	...	...	288	...	906	600	2,475
Gray slag, per cent. of charge	24	12	...	...	...	12	...	27	15	30
Gray slag, assay, per cent. lead	4	17–20	55	...	...	55	...	38	38.8	56
Of lead charged, recovered per cent., in bars	93	92.5	...	...	...	81	88	54.4	87.5	50
Recovered from gray slag and flue-dust	...	2.3	...	...	...	8	...	10	9.3	...
Total loss in lead	7	5.2	...	...	...	11	12	9[1]	3.2[1]	...
Outlay for labor, fuel and material per ton of ore of 2,000 lb. avoirdupois										
Labor, hours	90	61	36 aver.	20	...	15	12	8.4	11	9
Fuel, charcoal, pounds	...	...	...	...	...	...	...	...	...	...
Fuel, bituminous coal, tons	...	1.10	...	...	...	0.57–0.76	0.56	0.8–0.9	0.46	...
Fuel, wood, cords	1.60	...	1.10 aver.	0.83	...	...	...	...	...	...
Material, lime, pounds	...	...	...	...	...	...	...	26	20	...

[1] Includes smelting residue in the blast furnace.

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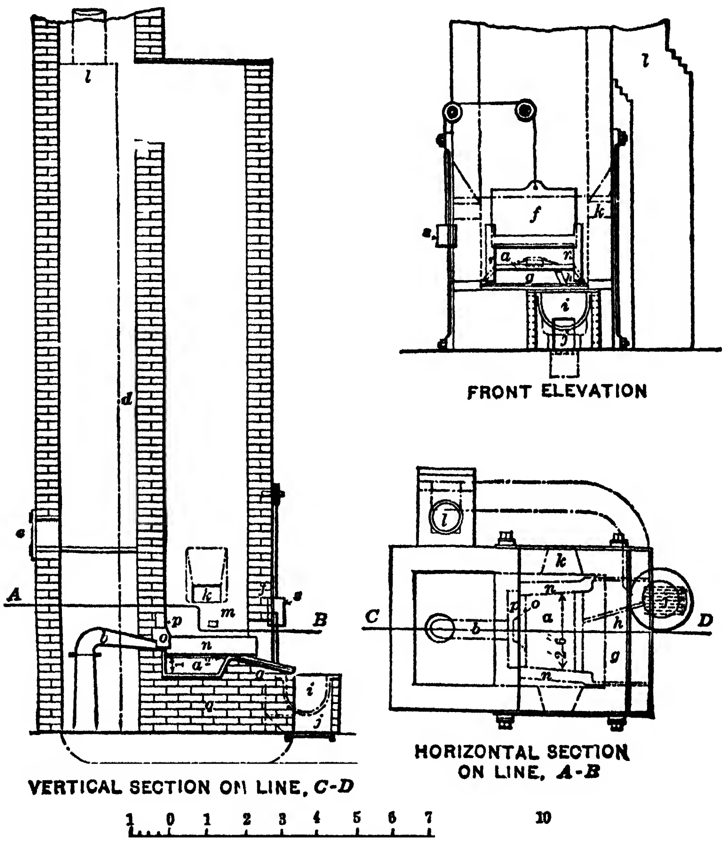
however, are even more strict than for the reverberatory; the Pb content (usually 70 per cent) should not be less than 65 per cent, the ore should be coarser (necessitating preliminary pugging or agglomerating, if too fine), and only low-silver ores should be treated. This last restriction is due to the fact that much lead and silver is volatilized, under the blast of the ore hearth. With the development of methods of recovery of dust and fume in baghouses and Cottrell plants, these volatilization losses are, of course, greatly reduced.



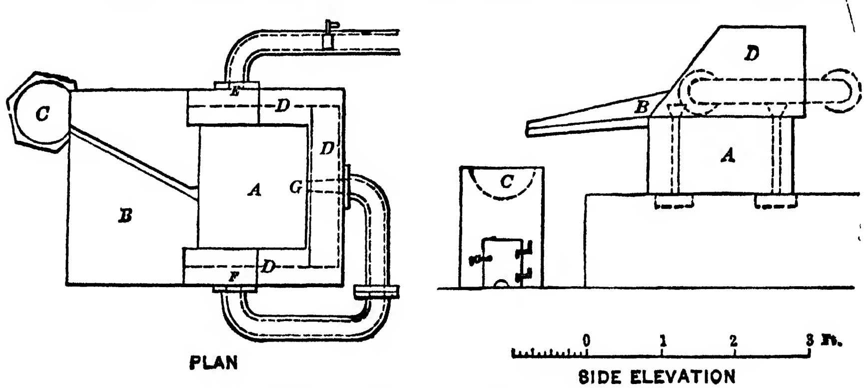
FIGS. 10-11.—Hand-operated ore hearth (English).

The ore hearth has one great advantage over the reverberatory—it is quickly started and stopped, without much loss of fuel or heat, and is, therefore, adaptable to the intermittent extraction of lead from small amounts of nonargentiferous ore. It also consumes less fuel than the reverberatory, but requires purer and higher grade ore.

On the nonargentiferous high-grade lead ores of the Mississippi Valley, the mechanical ore hearth is almost supreme, although one large smelting plant remains still an advocate of the blast furnace as a method of primary treatment. The other major smelter reduces galena concentrate of about 70 per cent grade to bullion and gray slag on mechanical ore hearths, utilizing the blast furnace only as secondary equipment for the smelting of gray slag. Both methods are conducted with high efficiency, and the blast-furnace procedure has ardent advocates, but the high-grade

ore of the district is peculiarly adapted to ore-hearth treatment. On ore of 70 per cent grade, or better, a 65 to 70 per cent lead extraction is obtained, as bullion, on the hearth; if the concentrate is 80 per cent grade, a 90 per cent extraction, or better, is possible, coke requirements being 3 to 5 per cent breeze. Of the lead charged, 15 to 20 per cent is rehandled as baghouse dust and fume, but this is largely $PbSO_4$ and PbO, which is of immense assistance in the ore-hearth process, which depends on the interaction of galena with the oxide or sulphate to form SO_2 and precipitate Pb. If there were a sufficient amount of oxidized product present to oxidize all the PbS, it would be possible, theoretically, to reduce and recover all the lead in both forms with but little extraneous heat.

About 10 to 15 per cent of the lead goes into a 50 per cent product—gray slag—which must be re-treated, and which makes an excellent material for rapid, efficient blast-furnace smelting. The Collinsville, Ill., plant, as will be seen from the blast-furnace table, using Newnam mechanical ore hearths (and blast furnaces for auxiliary treatment), maintained an abnormally high smelting speed on its blast furnaces, 7.9 tons of charge per square foot of hearth (blast-furnace) area, owing to the easy smelt-



FIGS. 12-13.—Rossie air-cooled ore hearth.

ing characteristics of gray slag which formed the principal constituent of its blast-furnace charge. On the other hand, it is to be noted that the Herculaneum plant with 80 per cent of its blast-furnace charge made up of Dwight machine double-roasted concentrate, and with no ore hearths or gray slag involved, has smelting speeds of 6.3 tons charge per square foot of blast-furnace hearth area. It has been found that the flotation concentrates of the Mississippi Valley, carrying 56 per cent lead, are not advantageously treated on the ore hearth, but must for maximum economy be double-roasted and smelted in the blast furnace.

The products of the ore hearth are similar to those of the reverberatory, with the added product of "browse," a mixture of ore, slag, and fuel, which goes back to the charge in the ore hearth.

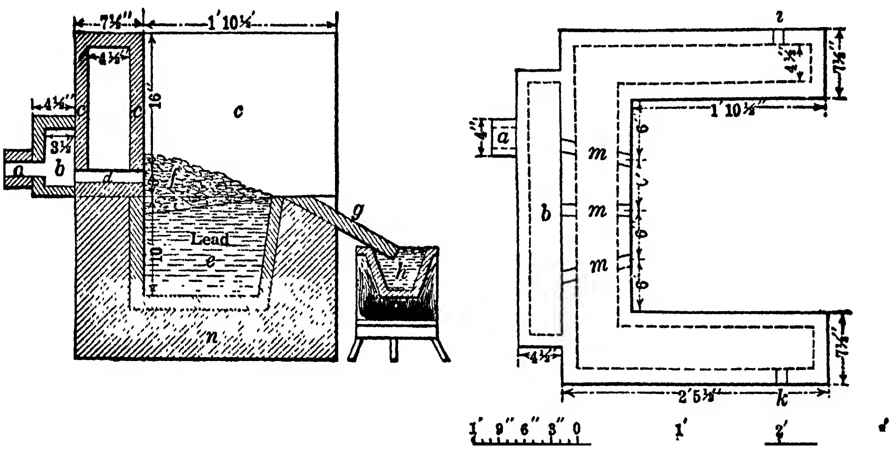
Being a simple type of metallurgical furnace, the ore hearth shows but little variety in construction or manner of operating. The four early hand-operated forms, shown in the accompanying illustrations (Figs. 16 to 20), differ somewhat radically from the mechanical furnace, the Newnam hearth, shown in Figs. 21 to 33.

Scotch Ore Hearth.—Figures 10 and 11 show a furnace used in England. The cast-iron box *a* set in brickwork *q* measures 2 ft. (front to back) × 2½ ft. (width). It is 1 ft. deep, and holds about 2 tons of lead. Work stone *g*, an inclined plate, is cast in one piece with the hearth box. Groove *h* leads the overflowing lead to kettle *i*, heated from fireplace *j*, the gases passing off through a flue into chimney *l*. On either

side of the hearth box is a cast-iron block *n*, and another iron block *o* is at the back. This back stone is perforated for the tuyère *b*, entering the furnace about 2 in. above the surface of the lead in the hearth. *p* is an upper back stone, or cast-iron block; the fore stone *m* is small. Brick shaft *c* carries off the fumes; at the back is a pit *d*, or dust chamber, cleaned through door *e*. On the side of the shaft is feed door *k*, for introducing fuel and removal of slag crusts at tuyères. Charge is fed from the front. A shutter *f* is in place at the front of the hearth; sliding in a frame *r*, it is raised and lowered by counterpoise *s*.

Bituminous coal is used as fuel. After operating for 12 to 15 hr. the hearth becomes too hot and must be cooled for about 5 hr. before work can be resumed.

The Rossie, or Air-cooled, Hearth.—Figures 12 and 13 show an arrangement of ore hearth in which the sides and back are air-cooled. The cast-iron jacket *D* has an air space inside. Blast enters at *E*, passes through *D*, leaves at *F*, and is delivered to tuyère *G*. This cools the walls of the hearth and preheats the blast. The Rossie



FIGS. 14–15.—Original American ore hearth.

hearth could be used continuously, but the hot blast caused excessive volatilization, and this hearth was abandoned until recovery of fume became possible, when it was again brought into use.

Original American Water-back Ore Hearth.—Figures 14 and 15 show the water-cooled ore hearth, in which work is continuous, owing to the cooling of the sides by water, which enters at *i* and passes out at *k*.

Modern American Water-back Ore Hearth.—In this furnace the cast-iron hearth box is supported by short columns in order to air-cool the lead; the upper sides are two water-cooled castings; the inside working length covers about 4 ft,; and two hoods are provided, an inner smaller one for carrying off dust and the bulk of fume by means of a suction fan, and an outer one for removing the remaining fume by natural draft. Such a furnace is shown in cross section (in Fig. 16).

Moffet Ore Hearth.—Figures 17 to 20 show the combined water- and air-cooled hearth, in double form, *i.e.*, two hearths placed back to back, under one hood. A water box cools the hottest part of the furnace, and upon this rests the air box, consisting of two separate chambers where the heated blast passes down through the water box by means of fourteen 1-in. copper tuyère pipes, seven on a side.

Newnam Mechanical Ore Hearth.—The hand hearths have all given way to the Newnam mechanically rabbled furnace, shown in Figs. 21 to 35. Figures 21 and 22

give a front and side elevation; Figs. 23 and 24, horizontal and vertical sections of the lead basin; Figs. 25, 26, and 27, elevations and sections of middle water jacket; Figs. 28, 29, and 30, elevations of right and left end jackets and section of right end jacket; Figs. 31, 32, and 33, details of cast-iron stand supporting the lead basin; and Figs. 34 and 35, perspective views of the furnace with rabbling mechanism at beginning and end of trip.

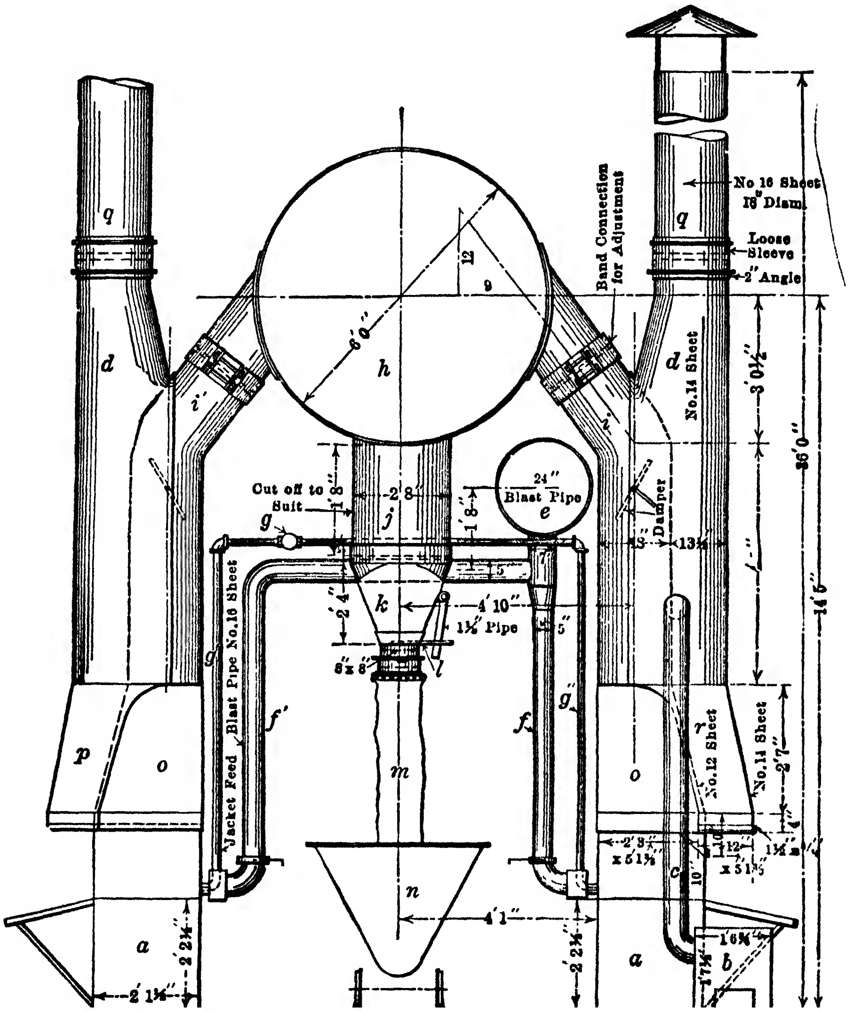
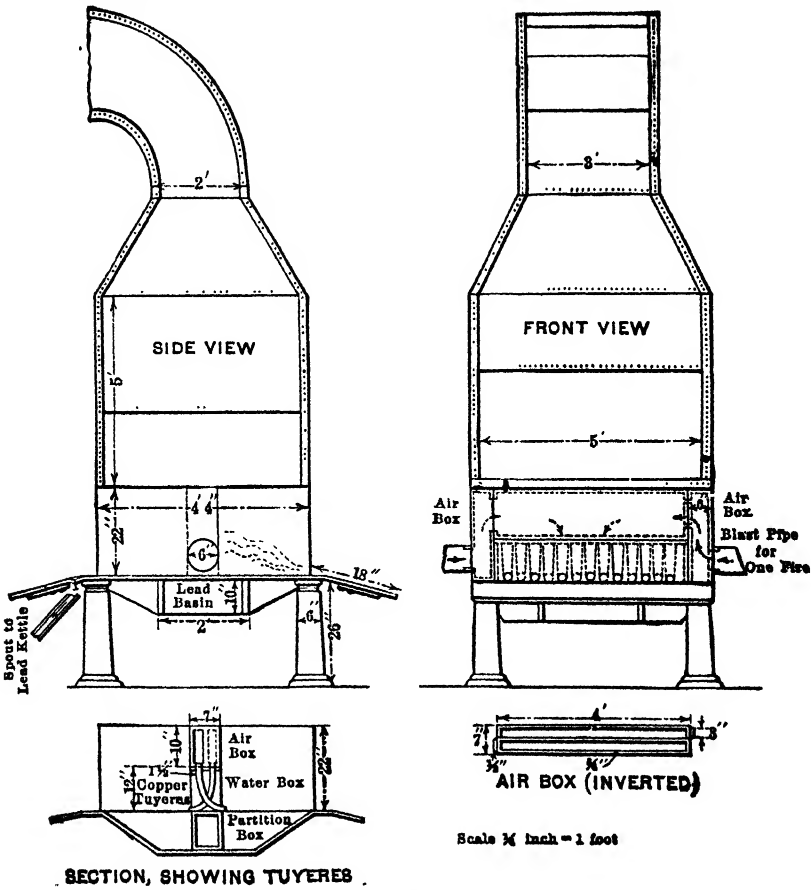


FIG. 16.—Modern American ore hearth.

The basin of the Newnam hearth shown is 8 ft. long, 19.5 in. wide at the top, 10 in. at the bottom, and 10 in. deep. The furnace has 12 tuyères. Lead discharges from the basin through siphon tap e (Fig. 23). The furnace is shown in perspective (Figs. 34 and 35), because the full assembly of detail drawings would be unnecessarily voluminous. The rabbling machine is hung from an overhead traveling carriage. This carriage starts from its position of rest at one end of the furnace. On the pulling of a lever, and during the trip to the other end, the rabble arm is given a motion similar

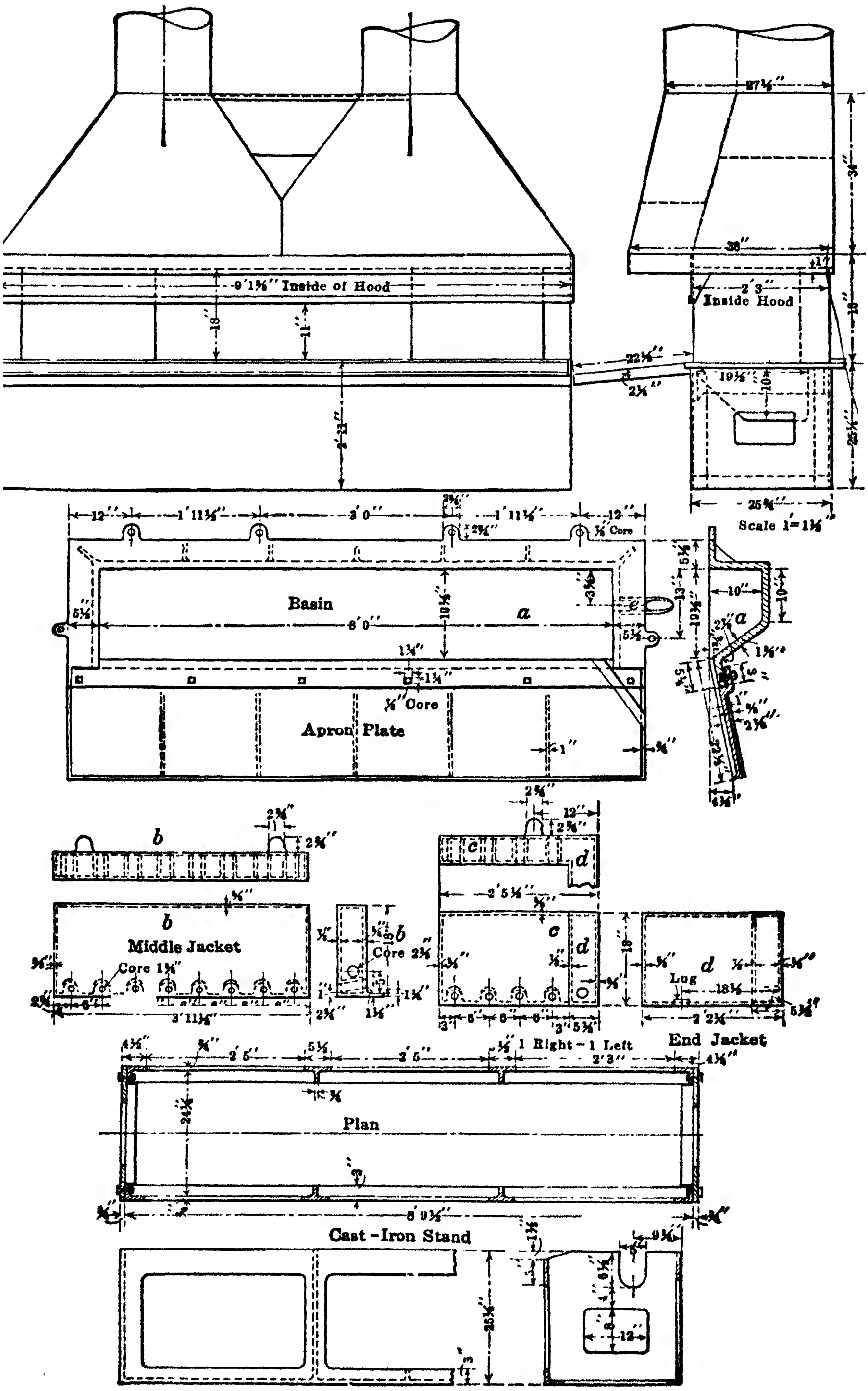
to that of the hand rabble. When the rabble arm is withdrawn from the fire, the carriage moves ahead 4 in. and starts the rabble on the next stroke. When the carriage reaches the opposite end of the furnace (Fig. 35), it is stopped automatically, the rabble arm withdrawn, and the carriage returned to its original position. A 1-hp. motor is sufficient for driving the axles of the carriage and the rabble arm.

The mode of operating with the Newnam mechanical hearth is the same as that in a hand-worked hearth, except that stirring is done by machinery. The first step in



FIGS. 17–20.—Moffet ore hearth.

the normal working of an ore hearth is to spread a few shovelfuls of coal over the fire, and then a thin layer of ore mixed with 0.5 to 1.0 per cent lime. The fire is left undisturbed for a short time—1 to 1½ min.—during which the charge is more or less oxidized, the flame breaks through, and the ore surface becomes crusted. The rabble arm thrusts over the edge of the basin into the lead and raises and loosens the slightly caked mass. As the mechanical arm rabbles the charge, one man follows it, pushes back the loose charge with a shovel, and drags the gray slag onto the apron plate. He is followed by a second man (charger), who transfers the gray slag to the water box, spreads a thin layer of ore onto the charge, and adds coke breeze as needed. By the time the trip to the end of the hearth has been covered, the ore first charged at the other end is ready to be rabbled.



FIGS. 21-33.—Newnam hearth.

The charge is made up of either galena alone, or galena mixed with sintered baghouse fume. Slaked lime was formerly used as a flux; with the substitution of coke breeze for bituminous coal, the greater heat generated has permitted the use of limestone. Fuel used ranges from 3 to 8 per cent of the ore mixture.

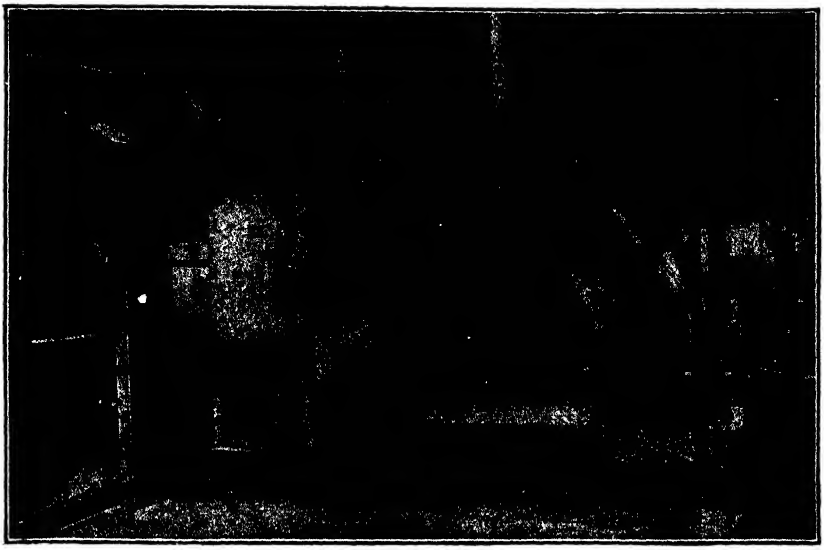


FIG. 34.—Rabbling mechanism—beginning of trip.

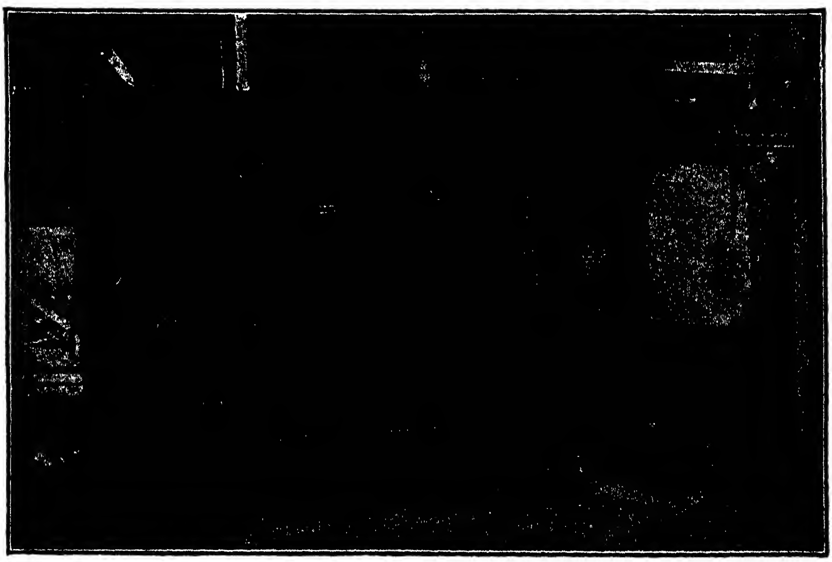


FIG. 35.—Rabbling mechanism—end of trip.

From the ore hearth the lead is collected in a pot, in which it is drossed. It is cleaned by liquating and poling, and is then cast into market bars, unless it is to be desilverized in the refinery. The yield in pig lead and the elimination of sulphur are

TABLE 6.—EXAMPLES OF SMELTING IN THE ORE HEARTH

Name	Date	Furnace						Products					Materials						Reference
		Front to back	Width	Depth	Sides, kind	Tuyères No.	Tuyères Diam.	Ore in 24 hr., lb.	Lead in 24 hr., lb.	Gray slag in 24 hr., lb.	Per cent lead direct from ore	Men in 24 hr.	Bituminous coal, lb.	Coke, lb.	Peat, bu.	Charcoal, bu.	Wood	Lime, bu.	
Rossie Works, N. Y.	1842	24"	24"	12"	Air-jacket	1	2"	9,988	7,389	.....	73.88	4	.....	.....	*	.....	¾	.....	(a)
Keld Head Mining Co., England	1870	23"	21"	12"	Cast-iron	1	. .	10,752	8,064	602	74.44	6	374	.....	12	.....	..	.....	(b)
Leadhill & Warlock, Scotland	1895	22"	30"	6"	Cast-iron	1	3"	......	6,720	.....	.....	6	500	.....	..	.....	..	.....	(c)
Weardale, England	1903	21"	27"	8–12"	Cast-iron	1	....	18,000	8,700	.....	61 00	..	.....	.....	*	.....	..	.....	(d)
Wanlockhead, Scotland	1912	22"	30"	6"	Cast-iron	1	....	.....	2,240	.....	60.00	6	560	.....	..	.....	..	.....	(e)
Granby, Mo.	1877	22½"	24"	11"	Water-jacket	3	....	9,000	7,500	.....	83.90	6	.....	...	.	27.6	.....	2 5	(f)
Hopewell, Mo.	1877	......	20"	12"	Water-jacket	1	....	6.000	1,464	.....	73.20	6	.....	.....	..	20.0?	.....	.....	(g)
Lone Elm, Mo.	1889	22"	48"	10"	Water- and air-jacket	7	1"	27,000	12,032	5,247	45.00	6	2,160	.....	.	.....	..	5.40	(h)
Granby, Mo.	1908	15"	4'	10"	Water-jacket	4	....	14,000°	......	2,000	75.00	4	*	...	..	....	..	*	(i)
Galena, Kans.	1909	......	5'	...	Air-jacket	10	....	21,000	...	....	50 00	6	*	.....	..	.....	..	. .	(j)
Granby, Mo.	1911	......	5'	...	Air-jacket	.	....	......	.....	.....	65 00	..	*	.....	..	.....	..	..	(k)
Webb City, Mo.	1911	18"	5'	7"	Air-jacket	10	....	14,000°	......	....	65 00	6	*	......	..	.....	..	6	(l)
Federal, Ill.	1914	18⅞"	4'	10"	Water-jacket	8	1"	22,500	7,200	.. .	60.00	6	.....	1,800	.	.....	..	....	(m)
Collinsville, Ill.	1914	18⅞"	4'	10"	Water-jacket	8	1"	21,000	6,200	.....	55 00	6	.....	1,680	..	.....	..	.....	(n)
Collinsville, Ill.°°	1923	19 5"	8'	10"	Water-jacket	16	1"	52,000[1]	24,400	9,000	67.00	6	. ..	2,600	..	.....	..	.....	(o)
Joplin, Mo.	1916	20"	5' 5"	. .	Air-jacket	..	....	28,000	12,600	4,200	60.00	..	1,200	.....	..	.....	..	.....	(p)
Galetta, Ont.°°	1917	19.5"	8'	10"	Water-jacket	16	1"	56,000[2]	33,000	8,000	75.13	6	.....	2,000	..	.....	..	1,000	(q)

[1] 19 tons concentrate, 7 tons by-products.

[2] 24 tons concentrate, 4 tons by-products.

* = used ° = works 12 hr. only °° = Newnam mechanical ore hearth.

(a) *Am. J. Sc. & Arts*, 1842, XLII, 169; (b) Percy, "Lead," 278–283, (c) Sexton, *Eng. Min. J.*, 1895, LIX, 175; (d) Middleton, *Eng. Min. J.*, 1905, LXXX, 10; (e) Correspondent, *Can. Min. J.*, 1912, XXXIII, 678; (f) Williams, "Industrial Report," p. 63; (g) *Ibid.*, p. 65; (h) Dewey, *Tr. A. I. M. E.*, 1889–90, XVIII, p. 674; (i) Perkins, *Eng. Min. J.*, 1907, XXXIV, 388; Buskett, *Min. Eng. World*, 1908, XXIX, 917; (j) Brinsmade, *op. cit.*, 1909, XXXI, 1029; Pulsifer, *op. cit*, 1914, XL, 450, 501; (k) Brown, *Tr. A. I. M. E.*, 1911, XLII, 402; Pulsifer, *Min. Eng. World*, 1914, XL, 450, 501; (l) Ruhl, *Min. Eng. World*, 1910, XXXIII, 1047; Wittich, *Mines & Minerals*, 1911, XXXI, 709; (m) Pulsifer, *Min. Eng. World*, 1913, ~~XXXIX, 375, 1914~~, XL, 450, 501; (n) Pulsifer, *op. cit.*, 1913, XXXIX, 681; 1914, XL, 450, 501; (o) Newnam, *Tr. A. I. M. E*, 1916, LIV, 485; (p) Brinsmade, *Min. Eng. World*, 1909, ~~XXXI, 1029~~; (q) Newnam, 1924, correspondence.

greater in the Newnam than in the hand hearth, the work easier and more healthful, and the cost much less.

Data from leading ore-hearth plants have been assembled (by Hofman) as shown in Table 6.

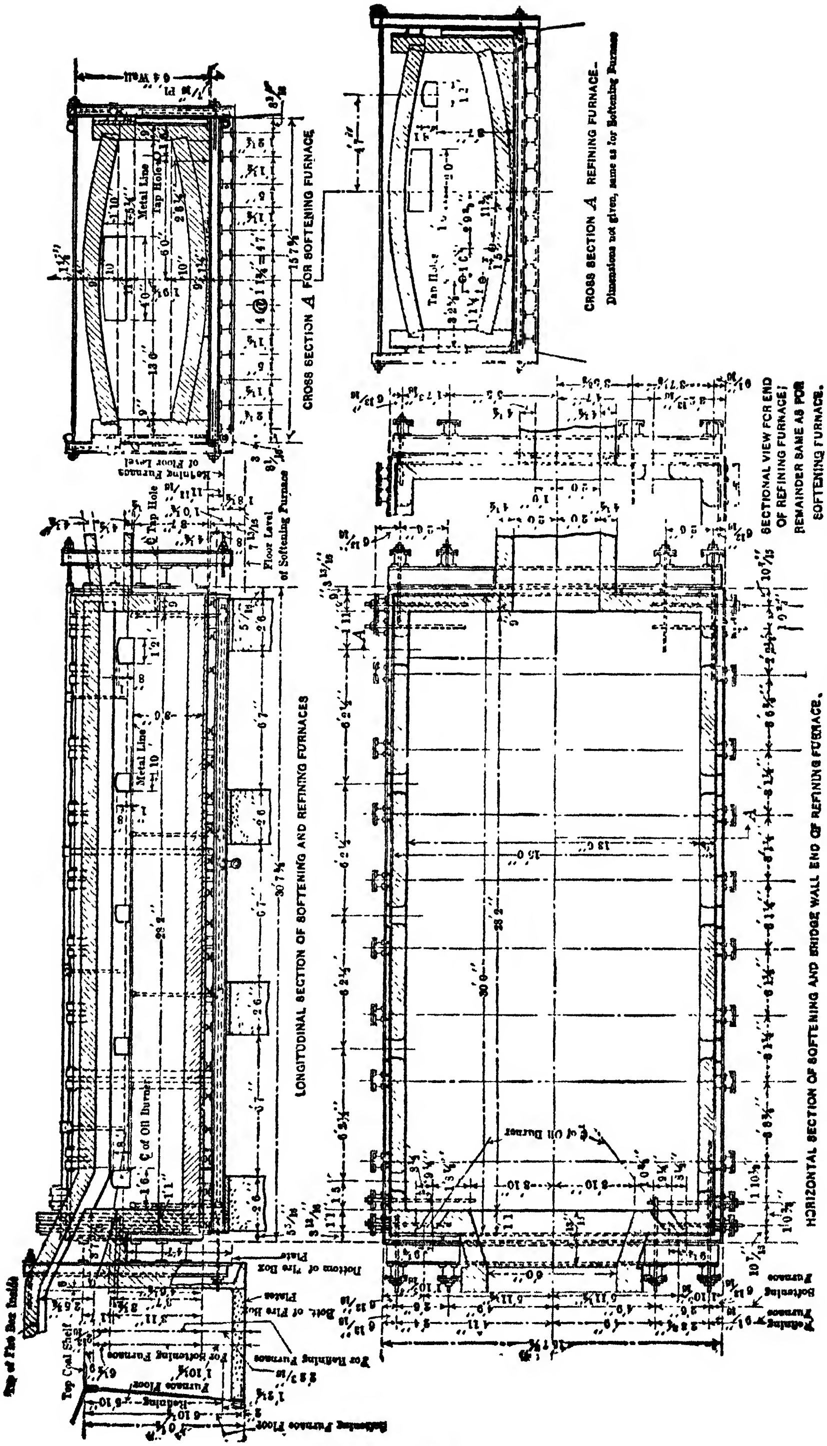
Desilverization and Refining of Lead Bullion.—The lead obtained from the ores of certain nonargentiferous districts—notably Missouri, Wisconsin, and a part of that from Spain and Germany—is comparatively free from silver as well as from base metals and can, therefore, be used in manufacture practically as it leaves the smelting furnace, after a simple "poling" or blowing with steam, followed by drossing. All the lead produced in blast furnaces from complex ores, however, contains at least enough silver to pay for extraction and, also, impurities which must be removed from the lead before it is fit for the market.

A desilverizing (refining) plant has for its task not only the separation of silver and the other precious metals (Au, Pt, Pd) from lead, but also the removal of the impurities Cu, Zn, Sn, Bi, As, Sb, S, Fe, Ni, Co, Te, and Se and the consequent concentration of a bullion carrying 95 to 98 per cent lead to a refined lead of not less than 99.73 per cent lead. These impurities themselves must also be worked up into salable products.

The standard methods of desilverizing and refining lead bullion are four in number: cupellation, Pattinson process, Parkes process, and Betts electrolytic process. Cupellation has ceased to exist as an independent process, but follows the processes of Pattinson and Parkes as an auxiliary. It can be adopted alone, however, in spite of its high losses and labor costs, for the treatment of rich lead in inaccessible districts where silver is the valuable metal sought. Up to the introduction of the Pattinson process, all argentiferous lead was cupeled; but costs and metal losses are so high that a limit is soon reached where the separation of silver by cupellation is not economical. This limit is at about 50 to 60 oz. silver per ton of lead. Below this grade, the silver recovered will hardly pay for the labor, fuel, and material used, the loss in metal, and the inferior grade of lead obtained from the subsequent reduction of the litharge produced in cupellation. It becomes necessary, then, to concentrate the silver into a smaller amount of lead before cupeling, and this is done by the Pattinson and Parkes processes. The process of desilverization must be preceded by a complete drossing of the furnace lead for removal of copper, either by poling and cooling or by the use of sulphur. This drossing is followed by a process of oxidation to remove other metal impurities. This oxidation is called "softening" in America and "improving" in England. The Parkes process must be followed by a refining or dezinking operation to remove the zinc left in the lead by the process, and to remove small traces of other impurities. Almost all the impurities in the furnace lead interfere, to a greater or less degree, with desilverization by either the Pattinson or Parkes processes. Generally speaking, the Parkes process requires a purer bullion than the Pattinson.

Arsenic and antimony are the most troublesome impurities, even when present in very small quantities. Next in order come tin, sulphur, iron, nickel, cobalt, and tellurium. Fortunately all these have a greater affinity for oxygen than lead and can, therefore, be largely removed by simple oxidation at a low red heat and a skimming of a molten bath.

Copper has less affinity for oxygen than the other impurities mentioned and is only partially removed by oxidation. It does form, however, an alloy with part of the lead itself, which is less fusible than pure lead, and resort is had to this characteristic to accomplish its removal in the ordinary drossing operation. Copper may be reduced to 0.002 per cent or less by treatment with sulphur, rapid agitation, and cooling to



FIGS. 36-39.—300-ton softening and refining furnace.

just above the freezing point of the lead. The copper is removed as sulphide with a considerable amount of lead in the form of a dry powdered dross.

Bismuth cannot be practically separated from lead by oxidation, as it has less affinity for oxygen than has lead itself. It does not interfere with desilverization but remains with the refined lead in the Parkes process. For most commercial uses of lead, bismuth is not an undesirable impurity; for some applications its presence in small amounts is very beneficial. For the production of white lead by the old Dutch process, however, its presence is undesirable, since it gives the product a gray color. The standard specifications for commercial grades (see page 145) limit the bismuth content of corroding lead, used for Dutch process white lead, to 0.05 per cent. Other commercial grades may contain up to 0.25 per cent bismuth. Removal of bismuth in the Pattinson process is not complete but is sufficient for some purposes. In the Betts electrolytic process, removal of bismuth is complete, since bismuth is not deposited on the cathodes but remains in the anode slime. Bismuth is reduced to 0.02 or lower economically by the Kroll-Betterton process by the use of magnesium and calcium as reagents.

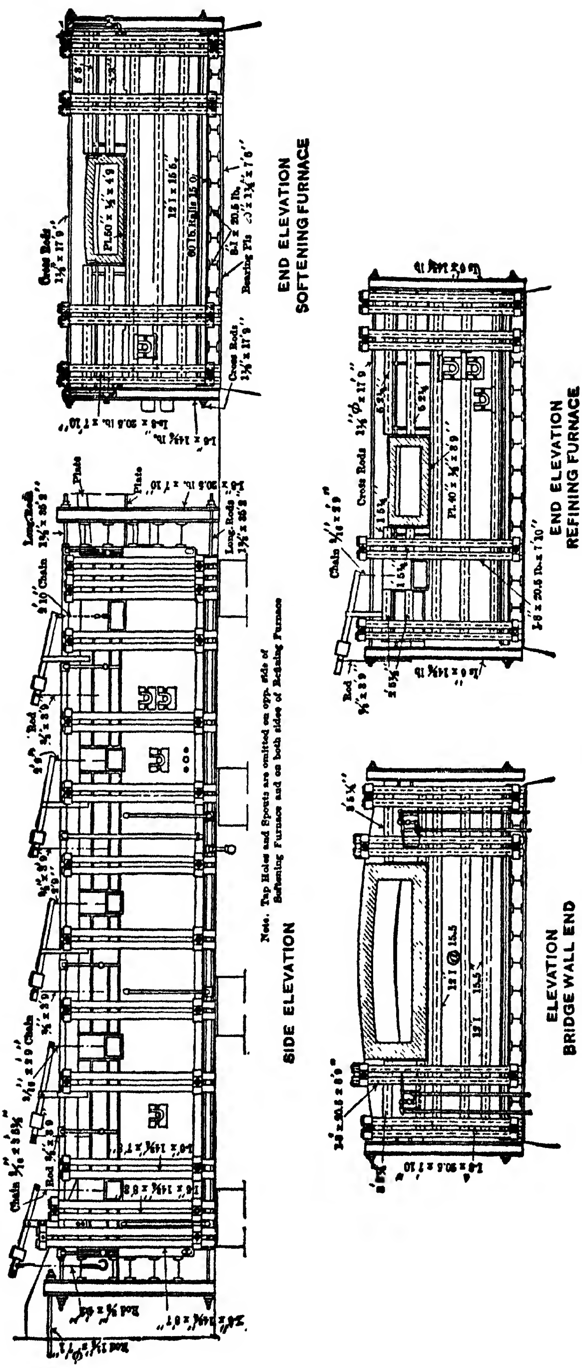
The many advantages that the Parkes process has over that of Pattinson have made it the preferred and most generally used desilverizing process in American practice. The Parkes method is lower in operating cost; produces market lead lower in silver content (0.10 to 0.20 oz. as compared with 0.40 to 0.60 oz. per ton by the Pattinson process); completely recovers even small traces of gold; produces a lead for cupellation with 2000 to 15,000 oz. silver per ton, as compared with 500 to 650 oz. by Pattinson; and shows a much lower loss of lead and silver.

A combination of the Parkes and Pattinson processes is sometimes used when bullion is high in bismuth, the desilverizing being performed by means of the Parkes process and the bismuth content of the desilverized lead being lowered by Pattinsonizing to 0.05 per cent, the dividing line between corroding and noncorroding lead. In more modern practice, combinations of the Parkes and the Kroll-Betterton process or the Betts process are used, which make it possible by combination of production to produce a range of bismuth content representing all commercial grades.

Softening.—The softening or "improving" of lead bullion as a preliminary to desilverizing by either the Parkes or Pattinson process is essential. This is partially accomplished in the drossing plants of lead blast-furnace smelteries which have no refinery on the premises and must therefore ship their base bullion to distant points for desilverizing. The major part of the softening operation is accomplished in any case at the refinery proper. In the Parkes process it has been shown that a decided saving in zinc consumption exists between the respective treatment of bullion that has been softened and bullion that has not been softened. For an unsoftened bullion containing 4.5 per cent foreign metals such as copper, arsenic, and antimony, 2.87 per cent zinc was required to desilverize the lead, whereas 1.75 per cent zinc sufficed if softening had preceded desilverization. The relative recoveries of market lead were 43 and 72 per cent of the bullion charged.

Softening has for its object the removal from the blast-furnace base bullion of the impurities that interfere with desilverization, mainly copper, tin, arsenic, antimony, and sulphur. Copper is best removed by a separate drossing operation prior to softening, but this operation is sometimes combined to some extent with the softening operation.

Furnace Softening.—The operation consists of two stages, liquation or drossing and oxidation. By liquation, metals held in solution by the furnace lead are separated from the lead by slow melting at a low temperature. By oxidation, which later occurs when the temperature is raised to a bright red with introduction of air or steam, metals alloyed with the lead are converted into oxides. These are to some



FIGS. 40–43.—300-ton softening and refining furnace.

extent volatilized, but mainly combine with the PbO, formed at the same time, and are slagged off.

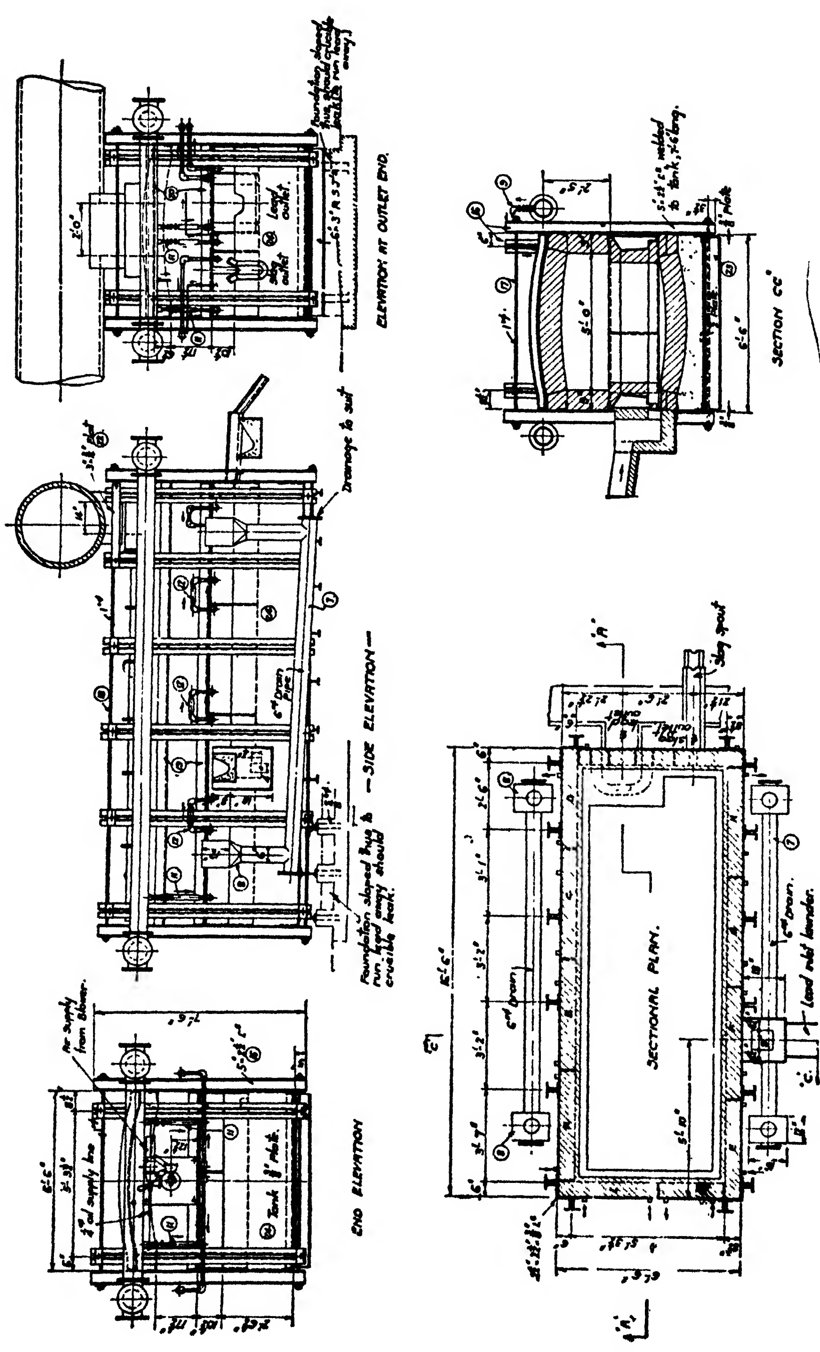
In the first step, the bullion is slowly melted at 370 to 380°C. and there rises to the surface a dross consisting principally of copper, sulphur, arsenic, and lead. In the second step when the temperature has been raised to a good red heat, the three principal impurities alloyed with lead are oxidized in the order tin, arsenic, and antimony. The surface of the bullion becomes coated with dark yellow powdery "tin skimming," mainly antimoniate and stannate of lead and antimoniate of tin. As soon as the tin skimming has been removed, the lead begins to give off fumes of arsenic and antimony, and arsenate and antimoniate of lead begin to form. These are drawn off together as an "antimony skimming" after the furnace has been cooled sufficiently to cause the skimming to solidify. The last traces of antimony come out with difficulty, and to hasten the process rich litharge from the finishing cupels can be stirred into the bath.

Jets of air or steam are introduced through perforated pipes, to stir the bullion and hasten the oxidation. Before the antimony has been removed, a sample of the bullion will "work," *i.e.*, it will show small greasy particles of revolving black skimming on the surface of the lead. As the softening approaches the end point, these globules disappear and a thin yellow litharge forms.

In the continuous lead-refining process developed at Port Pirie, South Australia, discussed in more detail later, furnace softening is carried on continuously in a comparatively small water-cooled reverberatory furnace into which bullion containing 0.80 per cent antimony and 0.30 per cent arsenic flows at the rate of 26 tons per hr., and from which softened bullion containing 0.03 per cent antimony and 0.0004 per cent arsenic and a slag containing 8.0 per cent antimony flow continuously. The mixture of molten lead and slag flows continuously through a heated forehearth where the two separate by gravity and are withdrawn separately in a molten condition. The temperature of the softening reverberatory is maintained at 760°C. Air is introduced through water-cooled pipes submerged in the molten lead, and the oxidation reaction supplies the greater part of the heat required for the operation.

Three softening processes are in general use. Chemically the process is the same in each; however, the difference in equipment and operation is considerable. These are (1) batch-furnace softening, (2) continuous-furnace softening, and (3) Walker process or kettle softening.

In (1), a batch of 50 to 300 tons of molten bullion is held in a reverberatory furnace and agitated with air or steam at about 650°C. until the arsenic, antimony, and tin are lowered by oxidation to the desired amount. The temperature is lowered, and the aoxides are skimmed off as a solid skim or semimolten slag. In (2), the molten bullion flows continuously through a small reverberatory heated to about 760°C. and is strongly agitated with air. The arsenic, antimony, and tin with some lead are oxidized to form a slag that is liquid at this temperature. The molten lead and slag flow continuously from the furnace to a heated forehearth where they are separated by gravity. In (3), the molten lead in batches of 100 to 250 tons is heated in kettles to about 675°C., covered with a layer of hydrated lime, and strongly agitated by mechanical stirring, or air is introduced below the surface. The arsenic, antimony, and tin are oxidized with some lead. The molten oxides are collected or "blotted" off by the lime, maintaining a clean metal surface for rapid oxidation. The oxide-lime mixture collects as a dry pelletized dust-free skim, which is skimmed off the surface of the lead. The metal of the kettle is protected by the use of lime from the corrosive action of the molten oxides of arsenic, antimony, and lead which would otherwise attack it at this temperature. This method may be applied to refining or dezinking lead with the same advantage, so far as protection of the kettle is concerned;



Figs. 44–48.—Details of softener, Port Pirie, Australia.

however, the amount of skimming produced is excessive, and the method has no economic advantage over other dezinking methods. As a softening method, it has proved very successful.

The furnaces used for softening and refining or dezinking in American practice are shown in Figs. 36 to 43.

The construction of the reverberatory furnace used for continuous softening at Port Pirie is shown in Figs. 44 to 59.

The fuel consumed in furnace softening ranges from 2 to 12 per cent, and averages 5 per cent soft coal, by weight, of the softened lead produced. Fuel oil is in some localities considerably more economical.

The time required for removal of arsenic and antimony by furnace softening varies with the size and design of the furnace, the temperature, the amount of air introduced, and other details of the operation. The rate of removal falls off as the impurity content is reduced. The total softening operation in practice includes of course the time of filling and emptying the furnace also. In general, it may be said that in a furnace of this capacity the complete softening of a charge of 200 tons of lead containing 1 per cent arsenic plus antimony will require 30 hr.

At Port Pirie a bullion containing 0.80 per cent antimony and 0.30 per cent arsenic is softened in the furnace illustrated at the rate of 26 tons per hr.

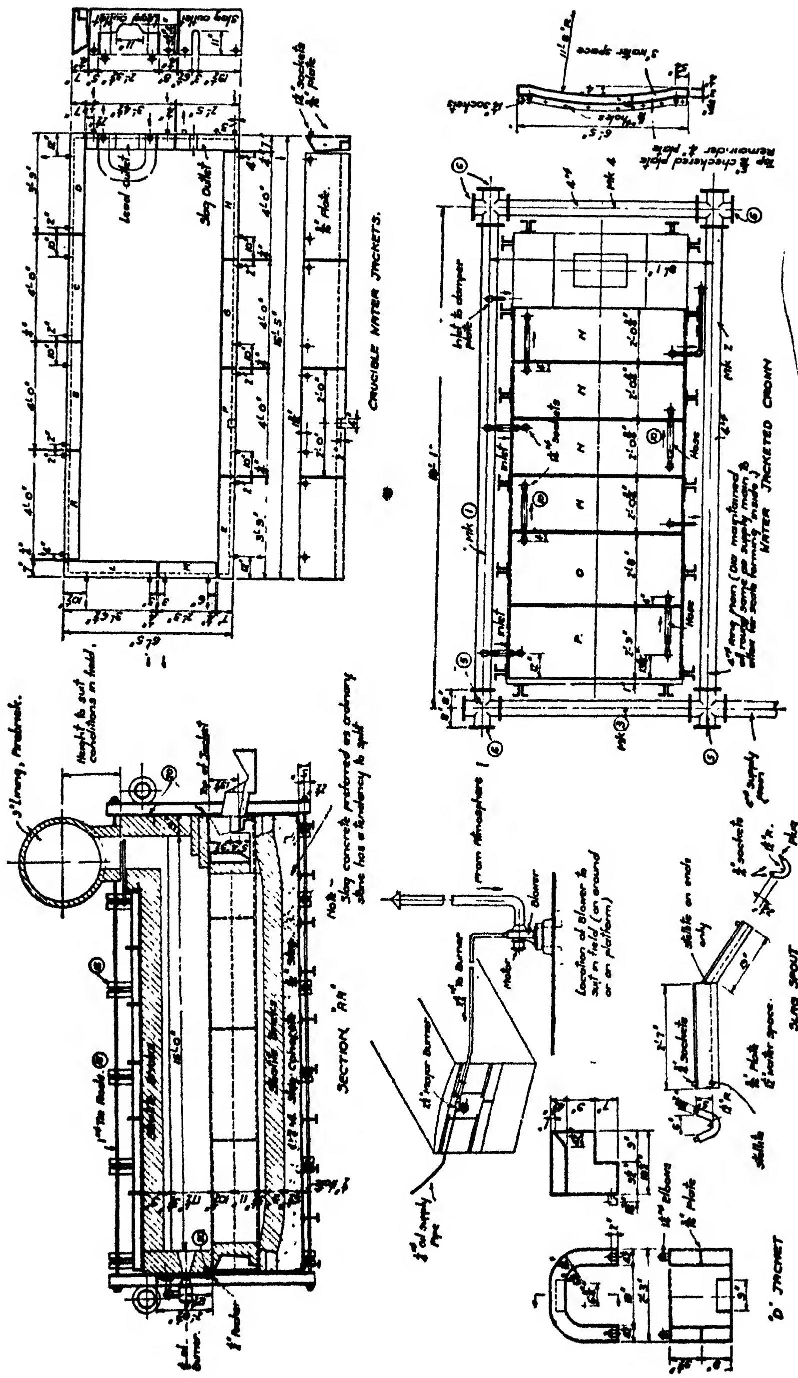
Colcord Process.—This process removes copper and arsenic from the bullion as the first operation in refining prior to softening. Sulphur is stirred into the metal with a mechanical stirrer at a temperature of about 350°C., which is sufficient to cause the sulphur to unite with the copper. The temperature is then raised to about 400°C. until the copper sulphide readily separates as a dross. The next step is to add caustic soda to the metal, raise the temperature to between 500 and 600°C., and thoroughly stir the caustic soda into the metal, using a mechanical stirrer, air jet, or other mechanical means. Arsenic contents of the metal can be reduced to any desired quantity by fractional additions of caustic. The sodium arsenate in the caustic skim is suitable for the manufacture of insecticides by leaching with water. The leached residue, containing lead and a little antimony, can be readily treated.

After the softening operation, the bullion goes to whichever desilverizing process is provided and the desilverized lead must then pass to a refining or dezinking treatment for the removal of the zinc remaining from the Parkes process (0.55 per cent), as well as the small amounts of arsenic and antimony that may not have been entirely removed during the softening or that were introduced with the zinc used in desilverizing. If the desilverizing has been by means of the Pattinson process, refining is sometimes necessary to remove the arsenic and antimony retained in the crystallized lead.

Harris Process.—The Harris process of softening and dezinking by the use of sodium hydrate is now in use at refining plants in England and on the continent, in Mexico, and in North Africa. This process is applicable to softening or dezinking of desilverized lead. It thus both precedes and follows the standard desilverizing operation by either the Parkes or Pattinson process.

The process is designed to accomplish the removal of such impurities as arsenic, antimony, and tin from base bullion or any other metallic lead material, and the removal of zinc from desilverized lead.

This is done by bringing about an intimate contact between the metal, at a temperature not greatly in excess of its melting point, and molten sodium hydrate. A clean separation takes place, thereby, of the lead from its impurities, arsenic, antimony, tin, and zinc, which are quantitatively collected in the form of their oxides or oxysalts, suspended in or otherwise associated with the molten caustic. The mixture of caustic and oxide is then treated by a wet process for the recovery of the contained



FIGS. 49–59.—Details of softener, Port Pirie, Australia.

reagents and of the oxides and oxysalts derived from the impurities removed from the lead.

The circuit of the wet process is closed and complete, rendering a recuperation of 95 per cent of the free reagents possible, which, in turn, are used again in the process. The impurities are also completely and separately recovered and are free from either lead or other impurities. Arsenic and zinc, the latter from desilverized lead, are directly obtained in salable form, the former as calcium arsenate, the latter as zinc oxide, while the recovered antimony and tin compounds can readily be reduced to metal. The essential feature of the Harris process is that a clean separation of the constituents of the bullion is made possible, each being recovered completely and in marketable form. The operation is all performed in, and above, the regular refinery kettle, without furnaces. The pumping apparatus and chemical-treatment tank is a portable unit which is swung onto the top of the kettle and removed when purification is complete.

In the usual design of this apparatus the molten mixture of caustic and other salts is contained in a small tank through which the molten lead is pumped and allowed to overflow and return to the kettle. The circulation of the lead through the molten reagent is continued until the desired purity is obtained.

The process is sound and practical in principle and has many advantages, but has not been universally adopted, since in practice it cannot always compete economically with other processes. Where it has been successfully applied, considerable modification has been necessary in most cases to adapt it to local conditions and materials.

Furnace Refining.—The furnace used for dezinking and refining is similar in construction and operation to the softening furnace, except that a higher temperature is required. The furnace is filled with desilverized lead containing 0.55 per cent zinc at a temperature of 450°C. The temperature is raised rapidly to 750°C., and steam is introduced through submerged pipes. The steam aids the oxidation by agitation and also by the decomposition of water by metallic zinc. The treatment is continued until the zinc and antimony are reduced by oxidation to approximately 0.001 per cent zinc and 0.005 per cent antimony. The zinc and antimony, with considerable lead, are skimmed from the surface of the molten lead in the furnace in the form of a dry powdery oxide skim, which changes to a molten slag at the end of the operation. For a lead containing 0.55 per cent zinc and 0.3 per cent antimony the operation requires 12 to 16 hr. and produces about 5 per cent skim, containing about 90 per cent lead. Corrosion of the furnace refractories by the refining skim is very severe.

Dezinking with Chlorine.—The chlorine dezinking process is the one most generally employed in the lead refineries in the United States. It has the advantages that the destructive corrosion of the refinery equipment is avoided and the zinc is recovered in a marketable product. The process is conducted in kettles using any one of several types of apparatus. One of these, the Betterton apparatus, is shown in Fig. 60.

The molten desilverized lead is heated to 450°C. in a kettle and is pumped through a chamber where it is brought into intimate contact with gaseous chlorine. The zinc contained in the lead is converted into zinc chloride, which separates from the lead and floats as a molten layer on the surface of the metal. The molten zinc chloride is removed from the surface, cleaned by treatment with metallic zinc, and marketed as a commercial chemical. The dezinked lead must be given a further treatment to remove antimony. This is done either by oxidation in a reverberatory furnace or by treatment with sodium hydrate in a kettle.

Molding Refined Lead.—Refined lead was formerly ladled by hand from the kettle into molds placed in front of it. This operation is now performed by mechanical equipment. The refined lead is run into molds either directly from the reverberatory

or kettle in which the zinc and antimony have been removed from the desilverized lead, or, as is more common practice with plants having large units, the refined lead is tapped into a storage reverberatory furnace or market kettle from which it is run or pumped into molds. The storage reverberatory is of the same capacity as the refining furnace, and its construction is similar, though it is not generally water jacketed.

A great variety of mechanical casting machines for pig lead have been developed and are in use. Each type is usually a local modification of a standard type, though some designs have become standardized and are sold by equipment manufacturers.

The three general types are the "straight line" or Walker type, the "vertical wheel" or Miller type, and the "horizontal wheel" or Newnam type. Much ingenious mechanical equipment has been developed for performing the various operations of skimming, trimming, stamping, and handling of the bars, and the labor required for the molding operation has been greatly reduced. With machines molding an average

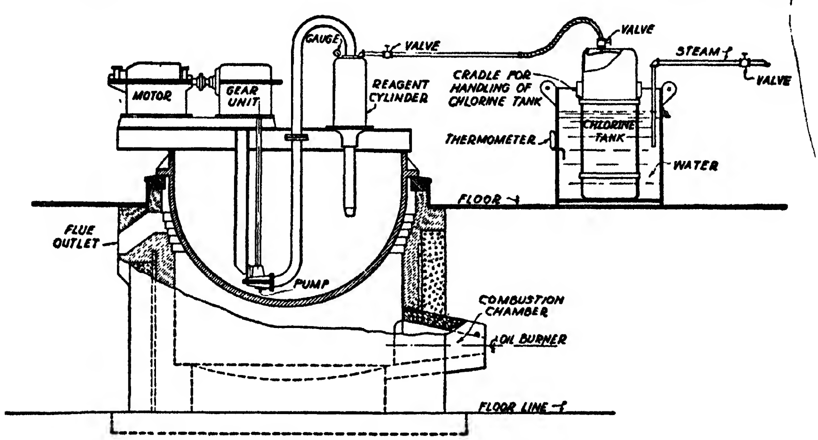


FIG. 60.—Betterton chlorine dezinking machine.

of 35 to 50 tons per hour, lead can be molded, weighed, and placed in stock or in cars for shipment with a crew of four men, one of whom operates a power truck.

Straight-line Molding Machine.—The lead is usually run from the furnace or pumped from a kettle through a pipe, provided with a regulating valve, into a cast-iron trough which tilts on trunnions. The side of the trough has a number of 1-in. spouts through which the lead flows into the molds when the trough is tilted by means of an air lift, thus pouring a number of bars, usually five, at one time. The molds are carried by an endless link-chain conveyer which travels in a horizontal direction in front of the pouring trough. The conveyer travels for a distance beyond the trough, where the lead in the molds may be skimmed by hand. The bars are then cooled in travel by water sprays from below and are trimmed and stamped by hand or by mechanical devices. The conveyer then passes up an incline and discharges the bars by inverting the molds. The bars fall onto a table or truck and are stamped and handled either by hand or mechanically. While some horizontal straight-line machines have been designed to start and stop, traveling each time the distance represented by a group of bars poured, this slows the operation of the machine and introduces mechanical difficulties in preventing vibration and roughening of the molten lead in the molds. For this reason the conveyer usually travels continuously, and the pouring trough is arranged to travel with the conveyer while pouring and to be returned to its original position at twice the normal speed by an automatic mechanism.

Vertical-wheel Machine.—The Miller casting machine consists of a vertical iron wheel with water-jacketed molds on its periphery. This machine handles 12 to 14 tons of lead per hour with three men.

Horizontal-wheel Machine.—The Newnam casting machine is a horizontal-wheel type of machine that handles 50 tons of lead per hour with four men. The molds are arranged in sets of five parallel pigs, supported radially on a horizontal-wheel structure. Five pigs are poured simultaneously. As the wheel revolves the pigs are cooled, trimmed, and passed under an automatic stamping machine. They are removed by a pig-pulling and stacking machine which lifts the pigs out of the molds in sets of five and places them in a stack of 35 weighing approximately 3200 lb. The

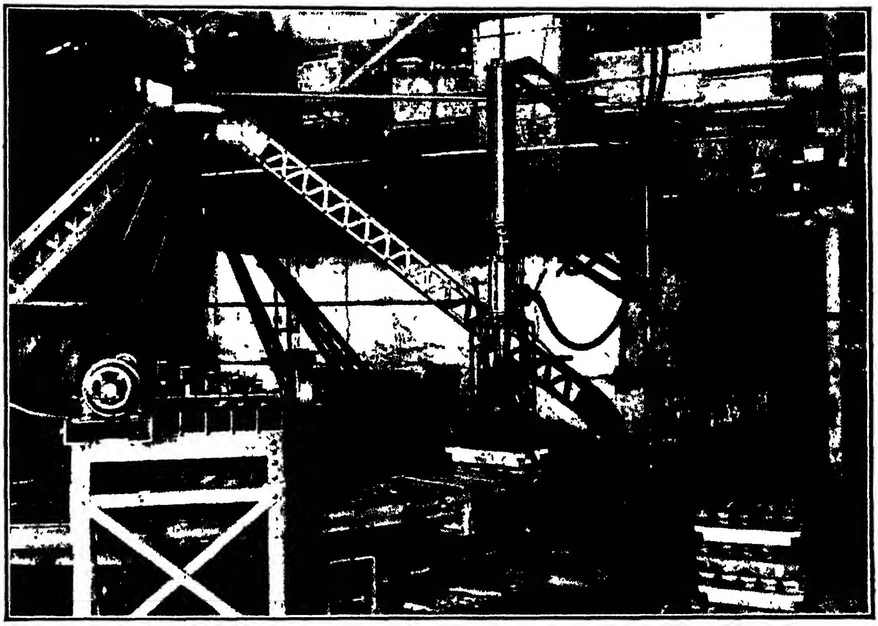


Fig. 61.—Five pigs just being lifted by Newnam pig-pulling and stacking machine.

stack is picked up by an electric truck of special design which, after passing over the scale, places the pile in stock or in a car for shipment.

The Newnam machine and lead truck are illustrated in Figs. 61 to 63.

Parkes Process.—This method of separating silver from lead is based on two facts: (1) a greater affinity of silver for zinc than for lead, and (2) the insolubility of zinc-silver alloys in lead which is already saturated with zinc. The process consists, in brief, of stirring 1 to 2 per cent of zinc into a bath of molten lead heated to above the melting point of zinc (415°C.) and allowing the mixture to cool, whereupon a crust rises to the surface of the molten lead containing nearly all the silver. A repetition of the zinc addition, in smaller quantity, gives another, lower, silver crust and leaves a molten lead that is practically free from silver, containing usually not more than 0.20 oz. per ton.

The zinc crust, which contains considerable lead besides the zinc and precious metals, is distilled in retorts for the recovery of zinc and to obtain an enriched retort bullion, which is cupeled to produce doré silver, with litharge as a by-product.

In addition to combining with silver, zinc has an affinity for other metals present, notably gold and copper, with both of which it combines before picking up silver.

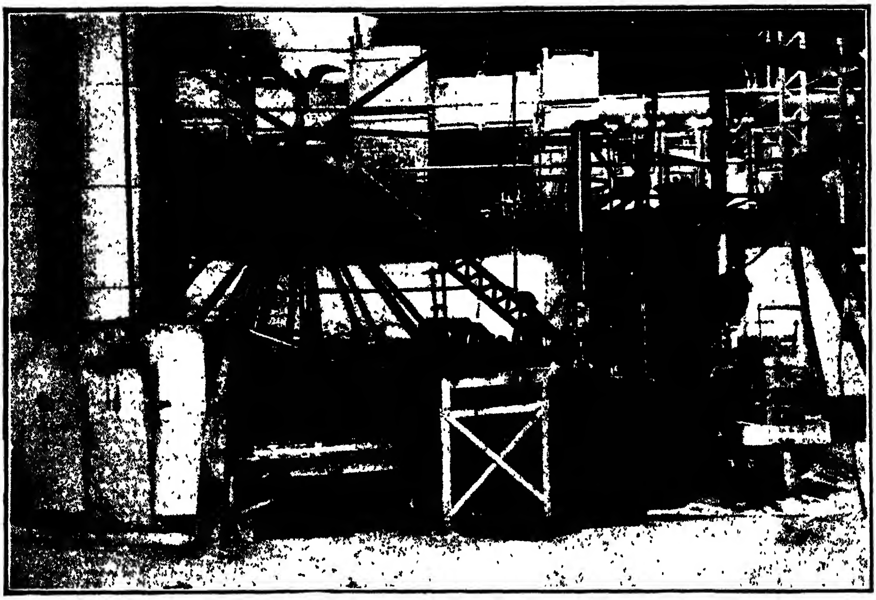


FIG. 62.—Casting wheel, cooling head, and head track.

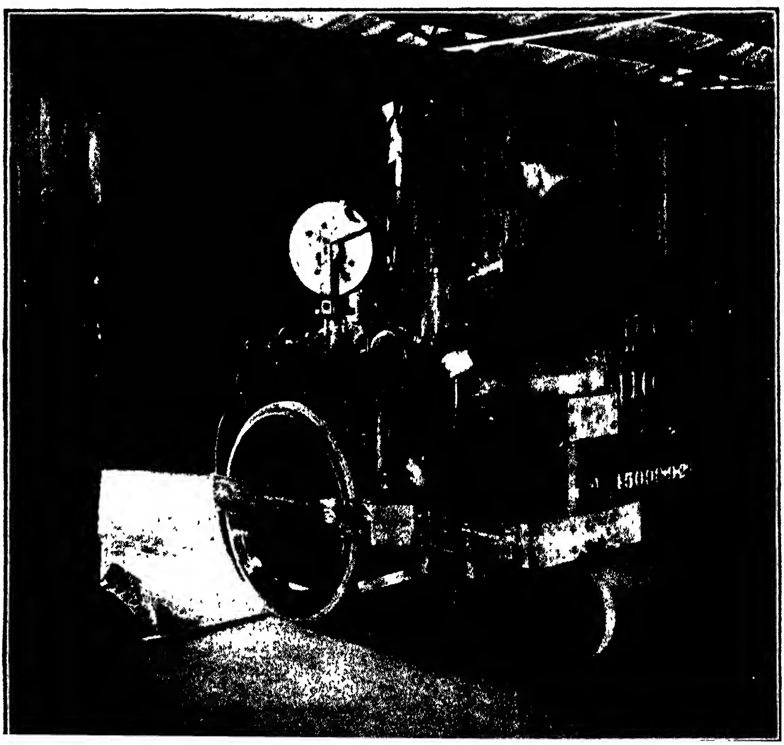


FIG. 63.—Newnam lead truck entering car.

Gold is entirely extracted by the first zinking, and copper enters the zinc crust almost as readily as gold, though not quite so completely. The gold-copper-zinc crust is formed, containing all but the minutest trace of the gold present, before the lead itself begins to take up zinc, the gold-zinc and copper-zinc alloys being apparently almost insoluble in zinc-free lead. It is impossible, in the case of silver, however, to produce a crust without first saturating the lead with zinc. The saturation point is approximately 0.55 per cent zinc.

Bismuth does not interfere with the desilverization, but antimony in amounts as small as 0.1 per cent, as well as arsenic in even smaller proportions, not only retards the rising of the crust but prevents a clean separation from the underlying lead. If the work lead contains 0.1 per cent antimony or 0.05 per cent arsenic, it is difficult to produce market lead sufficiently low in silver without excessive zinc consumption.

The importance of thorough softening is apparent. Arsenic, fortunately, is much more readily oxidized than antimony, so that it is completely removable by an 8- or 10-hr. softening, and the critical point becomes one of antimony removal. Copper is readily removed by repeated drossing or in the softening operation. If this has not been thoroughly accomplished, an excessive amount of copper-zinc crust is formed in the desilverization before any silver can be extracted. Nickel and cobalt have a tendency to enter the zinc crust like copper; however, both these metals are readily removable in the drossing operation.

In ordinary zinc desilverization, there are present, in varying amounts, besides silver, the metals gold, copper, platinum, palladium, tellurium, bismuth, arsenic, antimony, tin, nickel, and cobalt in the base bullion and cadmium and iron in the spelter. Of these, silver, gold, copper, platinum, and tellurium readily enter the zinc crust. The others do so only to a slight degree. They interfere, more or less, however, with the work, and the zinc consumption is usually increased by their presence. The quantity of zinc necessary to accomplish desilverization depends, of course, on the purity of the lead and the amount of silver present. If the lead is practically pure, it will hold in solution between 0.6 and 0.8 per cent zinc, at about 400°C. This quantity has to be added to the kettle as a constant, before the lead will give up any of its silver. Thereafter, the quantity of zinc required for combining the zinc with silver must be provided on a basis of the compound Ag_2Zn_3.

In practice, it is not practicable to desilverize high-grade lead bullion by a single addition of zinc. If no gold crust is made, it is fairly uniform practice to desilverize by means of two additions of zinc. The aim is to concentrate as much silver as possible, and all the gold, into the first crust, which will contain 2000 oz. or more of silver per ton. This crust is sent directly to the retorts. In the second zinking, an excess of zinc over that required for the amount of silver present is used. This is necessary if the silver is to be thoroughly removed from the lead. The resulting crust is unsaturated and is used to take the place of part of the fresh zinc needed in the subsequent first zinking. The second crust is low in silver content, and may go as low as 10 oz. per ton.

The gold is removed with the silver, the gold-silver-zinc crust is retorted, the retort bullion is cupeled, and the doré silver parted either with sulphuric acid or by electrolysis. The making of a separate gold crust is in most cases not economical, or usual in the United States, as it requires time and also separate storing and handling of two classes of products. The lead bullion also retains small amounts of gold in spite of the greatest care given to the gold-crust operation, and thus it is impossible to avoid the final parting of the doré silver produced.

For freeing the zinc crust from mechanically entrained lead, the Howard press is in general use, replacing the liquating kettles or reverberatory furnaces formerly used for this purpose. This press is described later and is illustrated in Fig. 64.

The desilverizing operation proceeds as follows: When the softened bullion in the kettle has been drossed and brought to about 482°C., blocks of crust from the preceding second zinking are charged and sufficient new zinc also is added. In some plants the blocks from the second zinking are charged first into the empty kettle, melted, and then the spelter added; following this the bullion is tapped into the kettle from the softening furnace and the mixture stirred to incorporate the zinc. In any case the crust and spelter must be incorporated into the bullion and the zinc brought into intimate contact with the metals gold, silver, and copper by thorough agitation. In some plants a small amount of ammonium chloride is thrown into the kettle before

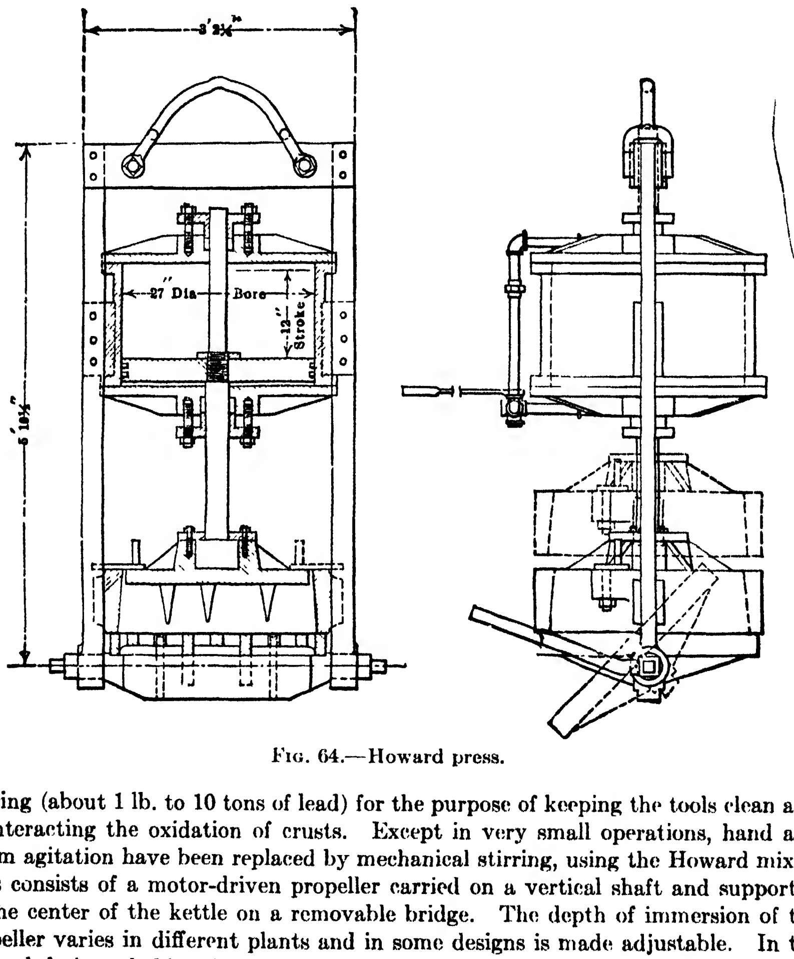


Fig. 64.—Howard press.

stirring (about 1 lb. to 10 tons of lead) for the purpose of keeping the tools clean and counteracting the oxidation of crusts. Except in very small operations, hand and steam agitation have been replaced by mechanical stirring, using the Howard mixer. This consists of a motor-driven propeller carried on a vertical shaft and supported at the center of the kettle on a removable bridge. The depth of immersion of the propeller varies in different plants and in some designs is made adjustable. In the original design of this mixer, the propeller was surrounded by a sheet-steel cone or cylinder open at top and bottom. In some designs this element is eliminated. The propeller is rotated to produce a downward flow of metal, and in operation a vortex is formed in the molten lead at the center of the kettle about the mixer shaft and a very thorough turning over and mixing of the metal is produced.

After stirring for 10 to 30 min. the first crust is removed and pressed. The second addition of zinc is then made and stirred in. The first crust is removed without lowering the temperature, which is held at about 450°C. since it is desirable to remove as

little lead as possible with the crust, and there is no attempt to clean the remaining lead of silver. In skimming the second crust, the temperature of the lead is lowered until all the crust that can be made to do so rises to the surface and is removed.

The weight of the crust produced varies with the amount of silver pressed. On a 100-ton kettle with 100-oz. bullion the first crust weighs approximately 7000 lb., and the partly desilverized remaining lead will contain 40 to 60 oz. of silver per ton. The second crust will weigh approximately 25,000 lb., and the desilverized lead remaining will contain less than 0.2 oz. of silver per ton. Two men in addition to the kettle

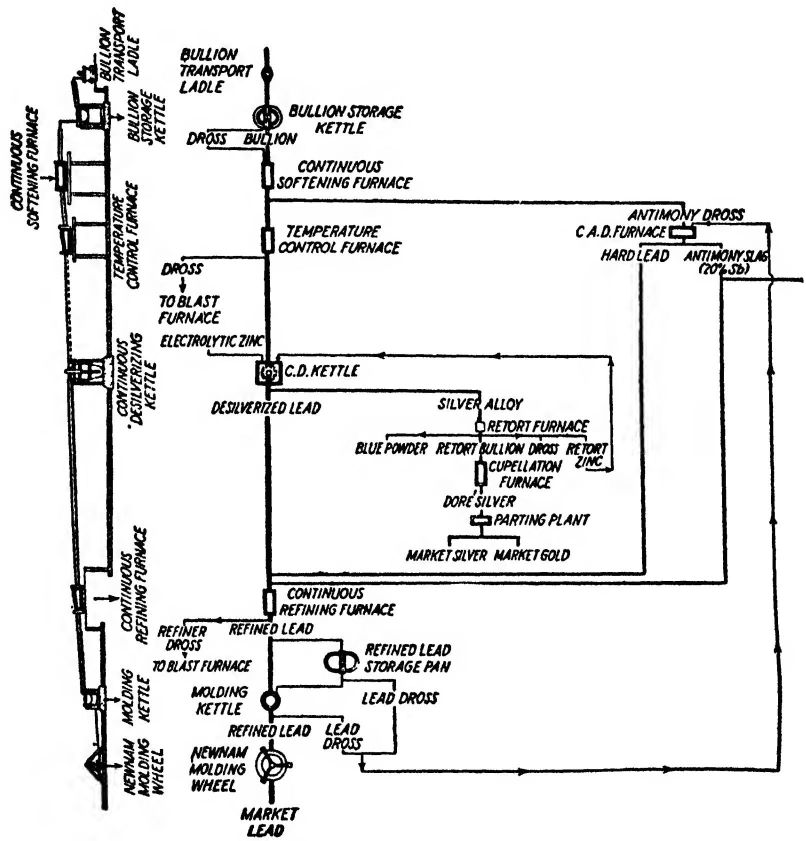


Fig. 65.—Flow sheet of continuous refining.

firemen usually do the entire work of desilverizing a single kettle of lead. About 2 tons of coal per 8-hr. shift is consumed.

Continuous Lead Refining.—At the Port Pirie plant of the Broken Hill Associated Smelters Proprietary Ltd., the operations of furnace softening, desilverizing by the Parkes process, and furnace dezinking have been combined and reduced to a continuous process in which the bullion flows continuously through these steps in succession and emerges completely refined. Slag, drosses, and other by-products are also withdrawn continuously and re-treated. A flow sheet of the process is shown in Fig. 65.

The softening furnace, briefly described under Furnace Softening, is a rectangular water-jacketed reverberatory fired with oil. The bullion enters and leaves the furnace

through submerged trapped openings. Molten slag overflows from the furnace continuously. Air is introduced through two water-cooled submerged blowpipes. The brickwork is of steatite bonded with sodium silicate.

Analyses of feed and products are shown in Table 7.

TABLE 7.—PORT PIRIE CONTINUOUS SOFTENING

Material	% Sb	% As	% Cu	Ag, oz.	Au, oz.
Drossed bullion to furnace	0.78	0.29	0.004	53.1	0.039
Softened bullion from furnace	0.03	0.0004	0.004	54.0	0.040
Molten slag from furnace	8.10	2.70	0.005		

The desilverizing kettles are of deep narrow form, resembling a bottle in cross section. They are approximately 20 ft. deep and 10 ft. in diameter at the widest point. Means for differential heating at different points in the kettle are provided in the setting, and definite temperature zones are maintained at different depths. The kettle is kept full of molten metal at all times. A practically constant range of composition and temperature is maintained from desilverized lead at 350°C. at the bottom to a layer of rich silver-zinc dross at 650°C. which floats on the surface. The molten softened bullion flows continuously to the kettle, entering at a temperature of 650°C. It passes downward through the zinc dross and various layers of molten metal, losing its silver content in the passage, and is withdrawn continuously from the bottom of the kettle through an inverted-siphon discharge pipe.

The silver-zinc dross is ladled out of the top of the kettle, concentrated in a liquating kettle similar in design to the desilverizing kettle, and is retorted and cupeled in the usual manner. The desilverized lead flows continuously to a rectangular reverberatory furnace similar to the softening furnace, is dezinked by oxidation, and flows continuously to a Newnam molding machine.

The continuous process requires a constant supply of bullion of uniform composition and produces a uniform product. It has the advantage of compactness in plant design, small stocks of by-products to be stored, and economy of labor required.

Equipment Used in the Parkes Process.—The kettles used in lead-refining operations may be constructed of cast iron, cast steel, or welded steel. They are usually of approximate hemispherical form and occasionally are elliptical. They range in capacity from 30 to 300 tons. Kettles up to 30 tons in capacity are usually made of cast iron. Larger sizes were formerly cast but in modern practice are made of welded steel plate up to 2 in. in thickness. The steel construction has the advantage of a thinner wall for heat transfer and also the fact that cracks or flaws may be repaired by welding, giving the kettle a long life in service.

Howard Stirrer.—The Howard stirrer or mixer is used for agitating molten lead when introducing zinc in the Parkes process or other reagents used in refining operations. It consists of a motor-driven propeller supported on a vertical shaft and submerged in the molten lead. The propeller is sometimes surrounded by a short cylinder or cone, open at the top and bottom, the upper rim of which is below the surface of the lead. The whole is supported on a frame bridging the kettle. The rotation of the propeller creates a vortex and a downward flow of lead at the center of the kettle. Any reagent to be mixed with the lead is drawn into this vortex, driven below the surface, and very thoroughly mixed with the metal.

Howard Dross Press.—The Howard press used for freeing dry drosses of mechanically entrained molten lead consists of a vertical frame supporting a vertical compressed-air or steam cylinder mounted above a shallow cylindrical receptacle, or

"basket," with a drop bottom. The cylinder is fitted with a piston that may be raised and lowered, and the piston rod carries at its other end a plunger, or platen, that fits into the basket. In some designs the face of this plunger is provided with projecting prongs that penetrate the material being pressed and pass through holes in the bottom plate when the plunger is forced to the bottom of the basket.

In use the press is suspended over a kettle of molten lead having a layer of dross on its surface, the plunger is raised free of the basket, and the press is lowered until the rim of the basket is only a few inches above the surface of the lead. The dross is then skimmed from the surface of the lead into the basket until it is filled. The plunger is lowered and forced down under a pressure of 90 to 100 lb. per sq. in., compacting the dross and squeezing out a large part of the entrained molten lead, which escapes through holes in the bottom plate or around its edge.

To discharge the press, it is swung aside and the bottom plate is dropped, discharging the pressed dross in a cake on the floor.

Dross Basket.—A considerable amount of entrained lead may be removed from granular drosses by merely placing them in a perforated vessel and allowing the lead to drain. The vessel, or "basket," usually takes the form of a 60-deg. steel cone 3 to 4 ft. in diameter and perforated with ¾-in. holes. It is provided with a bail and a tail chain so that it may be tilted and dumped. The basket is suspended from a crane over a kettle of molten lead, and the dross is skimmed into it until it is filled. It is then lifted above the surface of the lead and allowed to hang and drain for a short time before being swung aside and dumped. The basket may be manipulated on the surface of the lead by the suspending crane in such a way as to skim the dross from the surface of the lead. The use of a vibrator on the dross basket, while suspended to drain, has been found to increase the removal of lead appreciably.

Removal of Bismuth.—Bismuth occurs with lead in most lead ores and follows the lead through smelting and refining operations, including desilverizing by the Parkes process, to the final refined lead. Commercial refined lead specifications set a maximum limit of 0.25 per cent bismuth in common lead. The presence of bismuth in lead within this range has practically no effect upon its properties for any application as a metal and is an advantage in that it improves the lead for certain alloys. When refined lead is used in applications where it is to be dissolved or corroded for producing chemical compounds, bismuth may be an undesirable impurity. This is particularly true in the production of basic carbonate white lead by the Dutch or the Carter process, where any impurity in the lead enters the white lead produced. Bismuth in such a case renders the white lead gray in color. For such uses "corroding lead," containing less than 0.05 per cent bismuth, must be used.

Bismuth is removed from lead with other impurities at one operation in the Betts electrolytic refining process. The Pattinson process of desilverization removes bismuth to some extent with the silver; however, the removal is incomplete and the number of crystallizations and the amount of equipment required have made this process uneconomical for both silver and bismuth removal.

The Kroll-Betterton process for bismuth removal by the use of calcium and magnesium secures a very efficient removal of bismuth and is well adapted for application to desilverized lead as a step following the Parkes process.

Both calcium and magnesium will remove bismuth from lead when used alone, but when used in combination the efficiency of each is increased. These metals form compounds Ca_3Bi_2 and Mg_3Bi_2 which separate on cooling and can be removed as dross, similar to the zinc crust in the Parkes process.

Desilverized, dezinked lead, containing less than 0.01 per cent arsenic plus antimony, is treated with equal quantities of calcium and magnesium which are added at about 425°C. and thoroughly stirred into the lead. Magnesium is added as metal.

calcium is added as a 3 to 4 per cent calcium-lead alloy. The amounts of calcium and magnesium required to lower the bismuth to 0.02 per cent are indicated in Table 8.

TABLE 8.—KROLL-BETTERTON PROCESS

Bismuth in original metal, %	Reagent required, lb. per ton of lead	
	Calcium	Magnesium
0.10	1.30	1.30
0.50	2.15	2.15
0.80	2.90	2.90
1.00	3.40	3.40

The dross formed is removed by skimming and is recirculated in two stages similar to the Parkes process. The drossed lead contains 0.02 per cent bismuth and 0.05 per cent calcium and magnesium. The reagents are removed by chlorination or oxidation.[1]

The dross is concentrated to about 50 per cent bismuth by liquation of lead and is then treated for production of refined bismuth.

Treatment of Zinc Crust.—Many methods have been tried for working up the zinc crust: distillation, smelting, cupellation, alkali-chloride fusion, steam oxidation, ammonium-carbonate leaching, but only one has survived—distillation of the zinc from the crust in a retorting furnace. This subject is treated more fully elsewhere in this volume.

Treatment of Intermediate Products.—Refineries tend to accumulate a large assortment of by-products that must be worked up into marketable products currently with the major operation. These intermediate products are described briefly below.

Softening Furnace Dross and Skimming.—The copper drosses from the softening furnace are usually not of great amount, since the lead bullion is usually freed from dross at the smelter. The drosses from the softener are ordinarily kept separate from the skimming. Where the dross is treated by itself, the procedure is a simple liquation in a small reverberatory. The furnace is charged and heated until the lead that liquates out of the dross forms a bath, on which the dry dross floats. When sufficient dry dross has accumulated, it is pulled out through the furnace door. The temperature is set low so that no dross is again melted into the lead. Dry dross recovered is smelted in the blast furnace; the lead goes to the softening furnace.

The treatment of antimony-softener skimming is an operation leading to the production of antimonial lead. This skimming is smelted in a reverberatory furnace with the addition of a high-grade galena or stibnite and fine coal. The metallic lead reduced from the skimming contains most of the precious metals. This lead, carrying about 1.5 to 4 per cent antimony, goes to the softening furnace. The matte produced, carrying copper, lead, antimony, and sulphur, is treated by concentration smelting. The liquated or refined skimming or slag, now carrying 15 to 20 per cent antimony, some arsenic and copper, and about 1 oz. of silver per ton, is usually removed as a liquid slag and goes to a blast furnace for producing hard lead, in which it is smelted with coke and metallic iron. In order to keep down the loss of antimony by volatilization, galena is sometimes added to the blast-furnace charge, its sulphur acting as a reducing agent. Only enough is added for this purpose so that no matte is formed.

[1] The use of magnesium and potassium together is covered by U. S. patent 2133327.

This addition of galena dilutes the antimony in the resulting hard lead. The antimonial lead ordinarily produced and marketed from this operation contains 15 to 18 per cent antimony. Antimony ore, either sulphide or oxide, may also be added to the blast-furnace charge. The hard lead finally obtained is usually drossed with

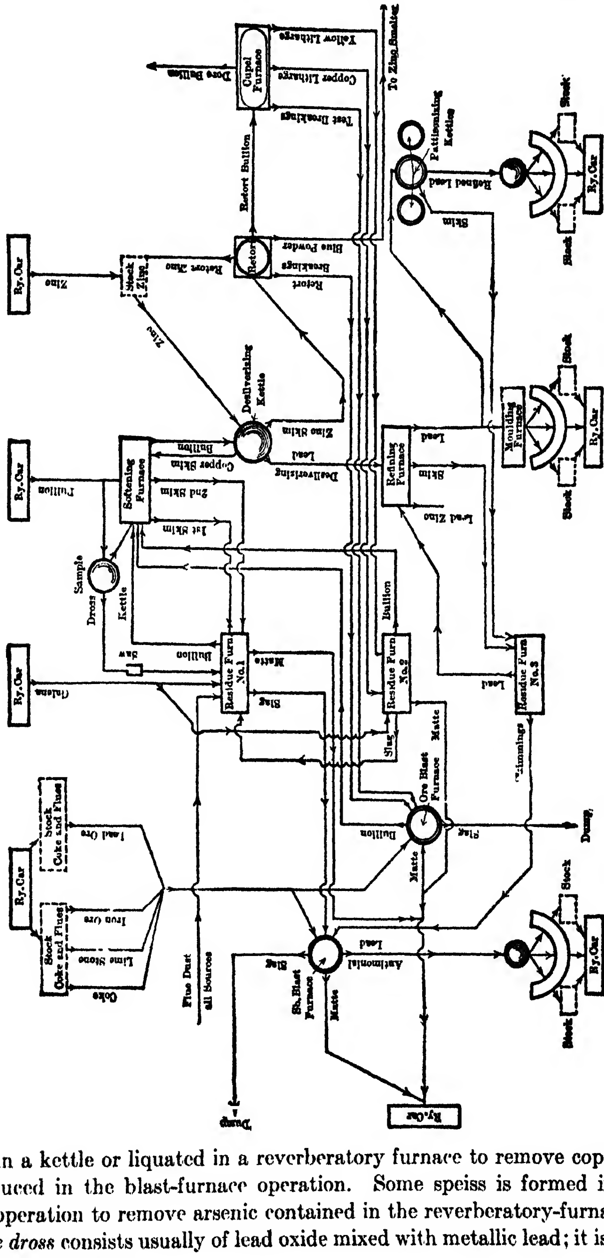


FIG. 66.—Flow sheet of lead smeltery and refinery.

sulphur in a kettle or liquated in a reverberatory furnace to remove copper that has been reduced in the blast-furnace operation. Some speiss is formed in the blast-furnace operation to remove arsenic contained in the reverberatory-furnace slag.

Kettle dross consists usually of lead oxide mixed with metallic lead; it is returned to the softening furnaces.

Refining skimmings and drosses carry 8 to 10 per cent zinc, some antimony, and about 75 per cent lead. Refining skimmings are sometimes charged into the softening furnace, after its dross has been removed, in order to assist in the oxidation of arsenic and antimony. Their high zinc content makes them refractory, and they are usually treated in a blast furnace where the zinc is slagged.

Metallic zinc recovered from the retorting of silver crust contains silver and lead as impurities and is returned to the desilverizing kettle as part of the zinc addition.

Retort dross is high in silver and zinc and is disposed of in one of two ways. In large refineries, where the retort bullion with its floating dross is poured into an operating cupeling furnace from the pot that has received it from the retort, the silver is of course recovered with the silver of the retort bullion. In smaller plants, this retort dross is worked off a little at a time in the regular cupeling, or in some cases it is charged back into the retorts itself. Accumulations of this dross are sometimes worked off on the bath of lead, low in silver, with which a new cupel test or hearth of the cupeling furnace is usually charged, in order to prevent excessive absorption of silver. Sometimes the retort dross is added to the softening furnace after the regular softener skim has been removed. This permits the silver of the retort dross to be taken up by the lead in the softener and the impurities to be oxidized into the skimming.

Blue powder is a mixture of metallic zinc particles and zinc oxide, with about 5 oz. of silver per ton, and is an awkward product for disposal, as it yields only some 50 per cent of its zinc on distillation by itself. At some plants it is returned to the retort with the next charge of zinc crust; at other plants it is added with the first zinc to the desilverizing kettle, where such metallic zinc as it may yield helps to saturate the lead with zinc and to assist in the removal of gold and copper. At other plants, it is disposed of by sale to zinc smelters or to chemical plants as a source of zinc for lithopone manufacture.

Litharge produced as a slag at the cupel is quite impure and contains, in addition to a considerable amount of silver, copper, antimony, arsenic, tellurium, selenium, and bismuth. It is preferably treated in a reverberatory furnace but is sometimes sent to the lead blast furnace.

Retort and cupel breakings are usually in large irregular pieces, containing considerable oxidized zinc, and are quite refractory; however, they usually contain a considerable amount of silver. Because of their refractory nature they cannot be successfully smelted in the reverberatory and are usually sent to the lead blast furnace.

Parkes Plant Layout.—The flow sheet of a typical efficiently arranged refinery using the Parkes process with a small Pattinson division, built for a monthly capacity of 5000 tons of lead bullion, is shown in Fig. 66.

The Pattinson Process.—This method of desilverizing lead is based on the fact that when molten low-grade silver-bearing lead is cooled to its freezing point, crystals of lead separate out that are much poorer in silver than the still liquid original lead. If these crystals are removed and the procedure repeated, always adding fresh lead of the same silver content, the greater part of the original bullion can be obtained in the form of market lead low in silver, leaving the balance in the form of an enriched lead ready for cupellation. By the repeated meltings and crystallizations involved, many of the impurities will be oxidized and collected in drosses, and the market lead will be correspondingly purified. A point will be reached eventually, beyond which the enrichment of the liquid lead cannot be carried. The process stops automatically, in practice, when the silver content of the liquid lead reaches 450 to 500 oz. of silver per ton; this material then goes to the cupels. The gold follows the silver through the process.

Of the base metals commonly found in lead bullion, antimony, nickel, and bismuth are also concentrated in the liquid lead; arsenic in the crystals; copper, which has

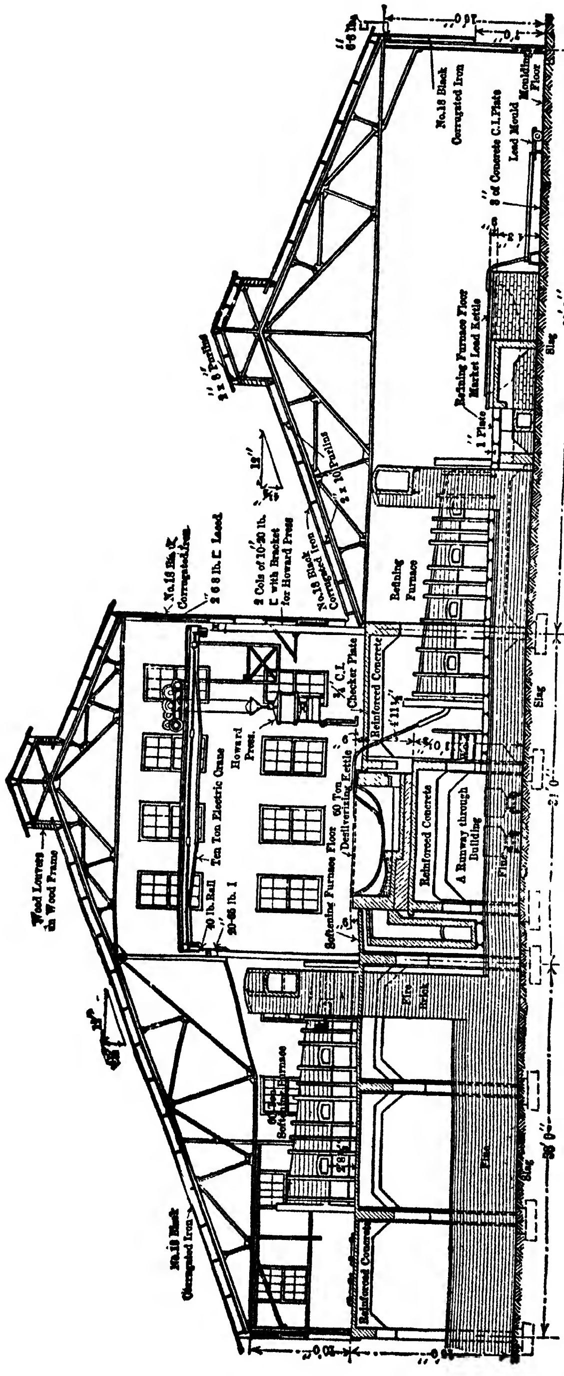


Fig. 67.—Parkes-Pattison plant, cross section.

not been removed in the softening furnace, or by drossing, remains equally distributed between the liquid and crystal lead.

The process may be conducted in one of two standard systems, the method "by thirds," or the method "by eighths." In the first and more common method, two-thirds of the metal in the kettle is withdrawn in the form of crystals, one-third remaining as liquid metal richer in silver. In the second method, seven-eighths of the metal is taken out as crystals, one-eighth remaining as liquid. The distribution of silver in the crystals and liquid in the two methods is illustrated in the examples below, which are taken from practice, except that the assays are rounded figures.

Original Bullion—100 Tons—56 oz. per Ton—5600 oz. Total[1]

"Thirds" Method	Weight, tons	Assay, Ag, oz. per ton	Total oz. Ag
Crystals	66 67	35	2,333.3
Liquid	33 33	100	3,333.3
Total	.....	...	5,666.6

Original Bullion—100 Tons—20 oz. per Ton—2000 oz.

"Eighths" Method	Weight, tons	Assay, Ag, oz. per ton	Total oz. Ag
Crystals	87.5	14	1,225.0
Liquid	12.5	60	750 0
Total	....	..	1,975.0

[1] Figures are from private notes of H. S. Levison, Am. Smelting & Refining Co.

The method by eighths was applicable only to bullions low in silver. With rich bullion the proportion of silver retained in the crystals became prohibitively high, and the method by thirds was more economical.

The original hand-labor Pattinson process was, until recently, in use in England and Germany. Machinery has been introduced to reduce the labor of withdrawing crystals and ladling out the liquid lead, the two principal mechanical modifications of the original process being the Luce-Rozan and the Tredinnick. In both, the metal is stirred by steam and the liquid drawn off, leaving the crystals in the kettle.

The procedure of the original process, using the method by thirds, is as follows: The kettles, varying in number from 8 to 15 according to the richness of the bullion, are arranged in a row, the position of the charging pot, or kettle in which the work lead is first melted down, varying in accordance with the proportion of silver in the lead. The pots are numbered in series, from the market lead end upward; the charging pot may be, in a series of 12 pots, anywhere between No. 6 and No. 10.

The melted bullion in the charging pot is poled and drossed, and the fire withdrawn and transferred to the next pot, in the melting stage. Crusts forming at the sides of the pot are pushed down into the lead to be remelted, and the bath is continuously stirred in order to ensure uniform cooling throughout. As crystals form, they are lifted, drained, and transferred, when dry, into a neighboring pot, usually "down the house," to the right. This continues until two-thirds of the contents of the charging pot has been removed, when the remaining one-third of still liquid lead is ladled into the adjoining pot, "up the house," to the left. If there is then on hand, from previous operations, lead equal in silver contents with that in these two right and left pots, respectively, an exactly similar operation is commenced with each of these simul-

taneously. The charging pot thus becomes filled from the crystals of the kettle at its left and the liquid lead of the kettle at its right. In this same manner the operations are continued, the kettles "down the house" decreasing in silver tenor and the kettles "up the house" increasing, until the silver content of the lead in the market kettle at the extreme right is 0.3 to 0.5 oz. per ton, and that of the liquid lead at the extreme left is at the maximum, about 500 oz. Before the whole plant can be in working order, a number of crystallizations must be performed in order to have on hand the necessary amounts of lead of different silver contents required to fill the several kettles.

The Luce-Rozan Method.—In this modification of the Pattinson process, steam is used for stirring, and the apparatus and the arrangement of plant are of radically

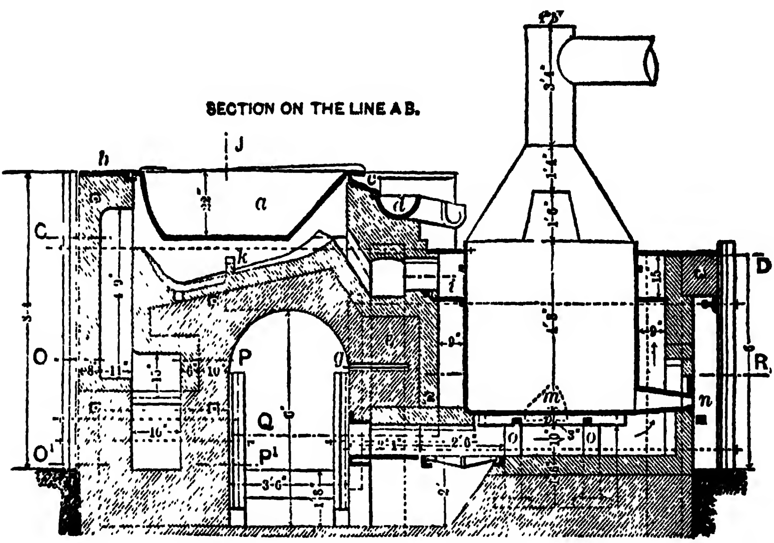


FIG. 68.—Luce-Rozan plant.

different nature. The plant is shown in Figs. 68, 69, and 70, and consist of two melting pans *a*, one crystallizing kettle *b* (Fig. 70), and two large conical molds, instead of the long line of some 12 kettles of the original Pattinson arrangement. The two cast-iron melting pans, used alternately, each holding 7 tons of lead, can be raised by means of a steam crane, so as to pour their contents into the crystallizer, which holds 20 tons.

The mode of working is as follows: The bullion is melted down in one of the melting pans, drossed, and run into the previously heated crystallizing kettles by raising the back end of the pan. In the crystallizer it is stirred by steam at 45-lb. pressure, cooled by withdrawal of fire and by water sprays, and two-thirds of the contents become crystallized. The still liquid lead is then run into the conical molds from the crystallizer, and the fire under the latter replaced and the crystals (13½ tons) remelted. In the meantime, 6½ tons more of lead, with the same silver content as that in the crystallizer, has been melted down in one of the pans, so that, as soon as the crystals have been remelted, it can be run in and a new operation begun. The other melting pan contains lead equal in silver content to the crystals that it is expected will be produced from the next operation, and this second pan is being melted down in readiness for the next following crystallization.

Eleven crystallizations are necessary to obtain market lead from lead bullion averaging 146 oz. of silver per ton. Six charges are run in 24 hr. Two men per shift attend to the crystallization; all lead handling is done by a crane man and helper. As in the hand Pattinson process, a number of preliminary crystallizations—66 at Pribram, Czechoslovakia—must take place to furnish the necessary intermediary grades of lead for normal work.

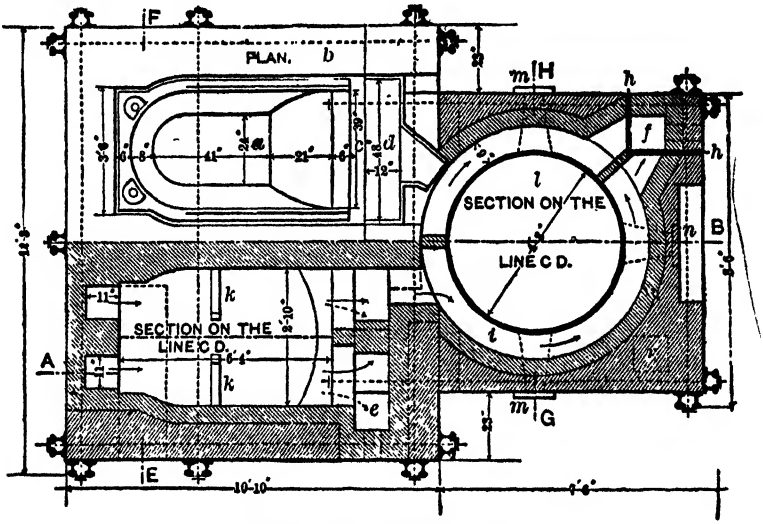


FIG. 69. - Luce-Rozan plant.

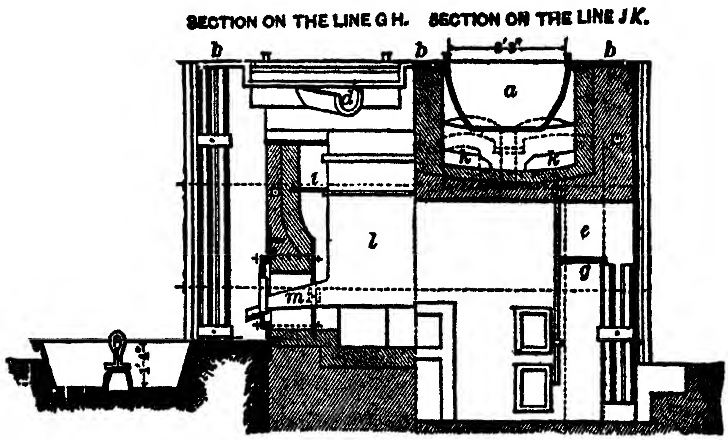


FIG. 70.—Luce-Rozan plant.

Products of the process (from above bullion) are rich lead of about 262 oz. of silver per ton, desilverized lead of about 0.43 oz. per ton, dross, and flue dust. The rich lead is cupeled, the desilverized lead is refined in a reverberatory furnace to remove arsenic and antimony and then molded into market bars, and the dross and dust are worked up with similar by-products from other parts of the works. A curious by-product sometimes encountered in the steam Pattinson process is a small incrustation of minium—red lead—which forms in the crystallizer, produced by the action of steam on the lead at a temperature just below redness.

The Luce-Rozan method runs into greater plant cost and maintenance than the original Pattinson, but its advantages more than offset these items. Softening of the lead bullion is not so imperative; the cost of labor is only 30 per cent, and of fuel 40 per cent, of the Pattinson cost; and only about one-third of the amount of drosses obtained in the Pattinson cycle is produced in the Luce-Rozan.

Other Pattinson Processes.—Several other variations of the Pattinson process have been developed and used to some extent. These do not introduce any new principles but differ in the equipment used and reduce the time required for the process very materially. These include the Tredinnick process and the Hall process. The Pattinson process is not used in the United States for desilverizing at the present time.

Cupellation.—The rich leads from the Pattinson process, containing 250 to 600 oz. of silver per ton, and the retort bullion from the Parkes process, containing 2000 to 5000 oz., are finally treated by cupellation for the separation of the precious metals. This process consists essentially of melting the rich lead in a reverberatory furnace and exposing it to a blast of air, by which the lead and the base metals are oxidized and slagged off in the form of litharge of varying degrees of purity, while the silver and gold, having scarcely any affinity for oxygen, remain behind in metallic state. The oxidation is accomplished mainly by the action ot the air blast and partly by the action of the molten litharge, which absorbs an excess of oxygen and gives it off to the underlying impurities Cu, As, Te, and Se. The cupellation of gold-silver-lead and the parting of doré bullion are discussed elsewhere in this volume.

CHAPTER VIII

TREATMENT OF ZINC CRUST AND ELECTROLYTIC SLIME

PART I TREATMENT OF ZINC CRUST PRODUCED FROM DESILVERIZATION OF LEAD BULLION

By T. D. Jones[1]

Introduction.—In this section the treatment of zinc crusts produced in the Parkes desilverizing process will be described. In the process of desilverizing, the refineries, if conditions warrant, can carry out a separate degolding operation, the crust being treated separately from the silver-zinc crust. However, in general, it is regular practice to remove the gold and silver in the regular desilverizing crust, paying particular attention to crust enrichment, so that at the present time so-called silver-zinc crust will assay 3000 to 8000 oz. doré per ton and 30 per cent zinc. The crust is then subjected to the distillation or retorting process for the recovery of zinc, which is returned to the desilverizing process.

Retorting.—The Faber du Faur type retort furnace is universally used for retorting. In former times the furnace was cubical in shape. However, many improvements have been made in construction so that at the present time the outside dimensions of the furnace are generally 3 ft. 10 in. in width and 4 ft. in depth, the over-all length being 6 ft. The furnaces are well-balanced tilting furnaces equipped with a suitable cast-iron shell which swings on trunnions. Modern furnaces are well insulated, the cast-iron shell being lined with suitable insulating material, the inner lining being of 9-in. fire-clay or high-alumina brick.

The arch of the furnace is so constructed that it follows closely the contour of the retort crucible in place. Every effort has been exercised in the firebox construction to provide conditions that would produce the maximum temperature adjacent to the retort crucible walls.

Retort furnaces are generally heated by gas or oil and are fired from the front or rear of the retort. While considerable controversy has existed over proper firing arrangements, experience has shown that the position of the burners has relatively no effect on the actual results obtained. The flue opening from the firing chamber is always on the same side as the burner, and this provides for sweeping action of the hot gases in order to obtain maximum fuel efficiency.

Formerly, the retort-furnace flues discharged into a large main brick flue and thence to a stack. Most recent installations provide for individual stacks of steel construction into which excess cold air may be drawn for cooling purposes. Usually, three individual stacks lead to a common header pipe, extending through the roof. This type of construction provides ample working space and excellent working conditions for the operators. Today, with modern construction and ventilation, retorting becomes a very desirable operating job, whereas, in former times, it was most unattractive to the operators.

The retort crucible, or No. 11 crucible, as termed by the manufacturer, is of standard shape and produced from select clays and Madagascar large-flake graphite.

[1] Traveling metallurgist, American Smelting & Refining Co.

Great progress has been made in details of retort construction, which, together with proper preheating facilities by the refineries, has increased retort life from 40 charges 10 years ago to 70 charges at the present time.

It is general practice to store retorts in hot drying chambers at the refineries and remove directly from the hot chambers to the retort stands as required. When setting the retort crucible, it is always good practice to provide a new stool or pillar, as a defective stool will cause the retort to shift during operation and breakage will result. The crucibles are usually set on the stools at an angle of inclination of 30 deg. from the horizontal. In this position, the crucible will have a capacity of 1300 to 1400 lb. of sized Parkes silver-zinc crust and also provide maximum heating area. The neck of the bottle is supported by brickwork, the top of the neck extending out 1½ in. from the face of the brickwork.

Considerable care must be used in starting retorts under fire. It is good practice to raise the temperature slowly, allowing approximately 8 hr. to reach maximum temperature. During this period, charcoal or other reducer must be placed inside the retort, in order to prevent excessive oxidation of the retort lining. It has been determined that the clay mix does not glaze over until a temperature of 1700°F. is reached, and unless a reducing agent is present during the heating-up period considerable life may be lost.

Condensers are usually of cast-iron construction, supported by a condenser stand. Modern construction provides for the condenser stand to be fastened to the furnace trunnion, and the stand swings in an arc and is held in place by a toggle hook. Suitable high-velocity ventilators extend over the mouth of the retort, in order to remove any escaping fume.

Once the retort has been charged and the condenser is in place, the minimum amount of fire clay or adobe for luting is used. Excessive use of adobe or fire clay causes the condenser to burn out.

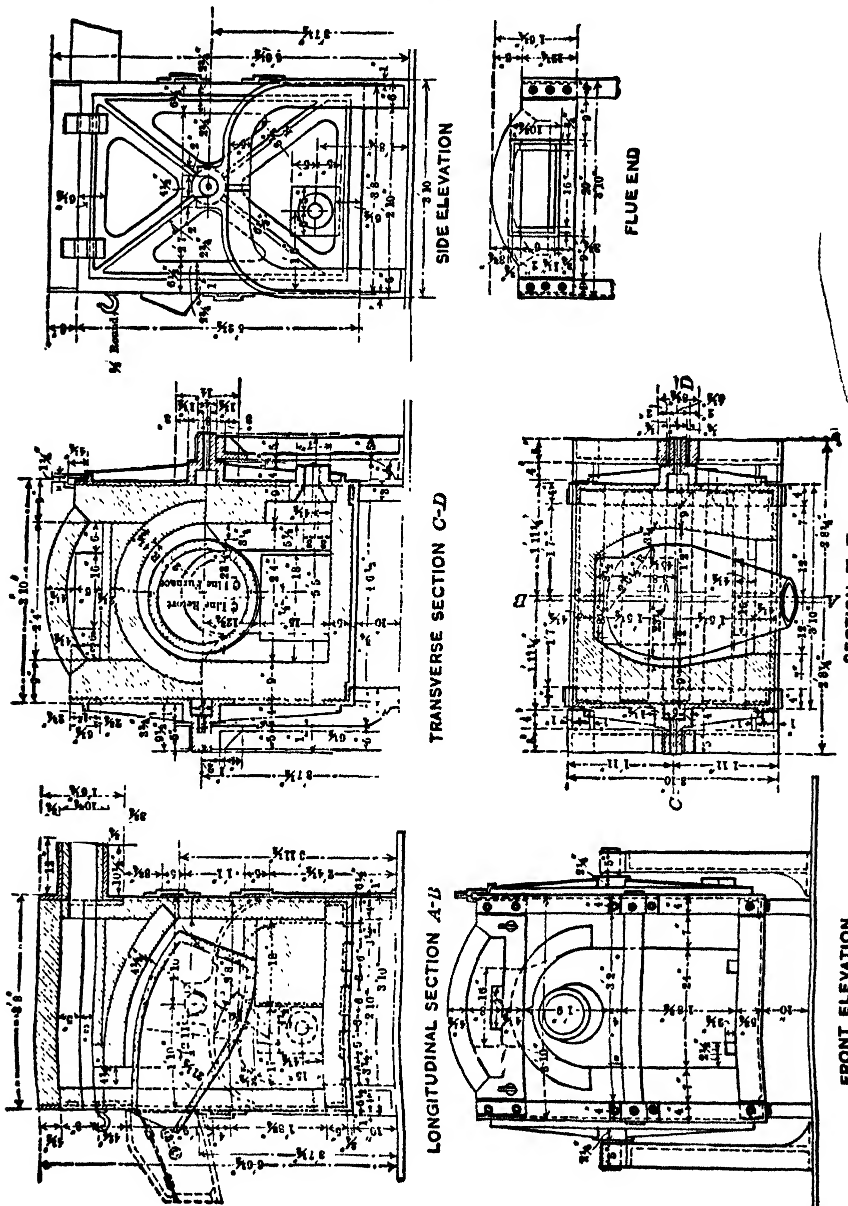
The proper operating temperature for retorting is approximately 1260°C., or 2300°F. Distillation requires 6 to 8 hr., and during this period approximately 420 lb. of zinc is distilled and cast into 50-lb. slab bars. Blue powder, approximately 12 lb. per charge, is formed during the operation, and the blue powder can largely be controlled by producing high-grade silver-zinc crust. Inferior silver-zinc crust containing much fine material requires a longer time for distillation, with subsequent increase in production of blue powder. The production of blue powder can be greatly reduced by adding flux with the silver-zinc crust charge. Still another practice to reduce the net blue powder produced is to screen the production, using totally enclosed shaker screens and returning the metallics directly to the retort charge, the end product, relatively low in doré, being shipped to a zinc smelter for recovery of zinc.

During distillation the condenser is of a cherry red color, and toward the end of distillation this color disappears and the condenser becomes dark in color, which indicates that the charge is nearly cooked.

The fuel oil required per ton of silver-zinc skim ranges from 40 to 60 gal., and where gas is used, the equivalent amount of B.t.u. is required. One man will operate three retorts per shift and at times can handle four retorts. The zinc in the final retort metal will analyze 1½ to 2½ per cent zinc. The retort metal assays 6000 to 14,000 oz. doré per ton, depending on pretreatment of silver-zinc crust prior to retorting.

Cupellation of Retort Bullion.—Considerable improvement has been made in cupel-furnace construction. While the old conventional type, comprising a removable test pan and stationary side walls and arch, is still in use, modern cupel construction consists of a sheet-steel shell resting on a tilting mechanism. The hearth, side walls, and arch are contained in the steel shell and are a complete unit.

While the old type test pan made from crushed limestone and fire clay usually had a life of 30 to 50 days, the new type cupels, having a high-alumina brick bottom, magnesite or high-alumina brick side walls up to the metal line, the upper side walls



FIGS. 1-6.—Oil-fired zinc-crust furnace.

and arch of fire-clay brick, will have a life of 6 months. The magnesite or high-alumina side walls and bottom will last 8 months with the aid of patching material, which is common operating practice.

Cupels in general are usually heated by oil or gas, the burners being located in the rear of the furnace directly opposite the charge door.

The new type cupels have a novel flue arrangement, the off-take flue being constructed of heavy sheet steel, built in sections which are adjustable. The off-take flue rests in position just over the charge door to the cupel, and sufficient extraneous air is drawn in with the hot cupel gases and fume to provide cooling, permitting the use of sheet-steel flues that have many advantages over the old-type brick flues.

The cupels are fitted with water-cooled jackets that serve to hold the breast of the cupel. The only reason for using water is to protect the breast material that is cut down by the operator during the cupeling cycle. A cupel is equipped with two or more tuyères, extending into the furnace through separate ports on either side of the burner ports. Compressed air at a pressure of 16 to 20 oz. is admitted through the tuyères in order to obtain rippling action on the surface of the bath. To obtain proper cupeling conditions, the tuyères are adjustable so that the air stream may be directed in any desired manner.

Cupels vary in size according to the doré output of the respective refineries. At the present time, cupels are capable of producing 100,000 to 350,000 oz. of finished doré per charge, the latter having outside dimensions of 7 ft. 11 in. in width and 10 ft. 2 in. in length, with a bath depth of 14 in. Where the larger cupels can be used, there is a considerable advantage, as the doré output per day, per cupel, is greatly increased, thus resulting in lower costs.

Under normal operating conditions, cupels are charged by adding cold bullion bars or hot charged from ladles containing hot retort bullion from the retorts. Bars or hot charges are added intermittently during the cupellation period until sufficient doré is present for a full doré charge.

The impurities found in retort metal are, as a rule, zinc, arsenic, antimony, copper, bismuth, and tellurium—a typical analysis being as follows:

DORÉ—6000 TO 14,000 OZ. PER TON

Impurity	Per cent	Impurity	Per cent
Zinc	1.5–2.5	Tellurium	0.2
Arsenic	0.4	Bismuth	0.25
Antimony	1.0	Lead	Balance
Copper	1.5–4.0		

The process of cupellation has for its object the separation of silver and gold from lead and the above-mentioned impurities. The operation of a cupel consists of first filling a cupel approximately one-half full of retort metal, melting down, and approaching a temperature of 2100°F. The tuyères are opened, and the bath is thoroughly rabbled in order to incorporate the zinky retort dross with the litharge formed during the early stages of cupellation. The thought is thoroughly to demetallize and desilverize the heavy drossy material which is relatively high in zinc.

The impurity zinc is readily oxidized, about 25 per cent going to the baghouse and 75 per cent collecting in the litharge. As soon as the cover slag thins down to the point where it can be removed from the cupel, the furnace is tilted and the zinky litharge drawn off through the breast to suitable portable pots or pans. As a cupel cycle may consume as much as 3 days, it is understood that current production of retort metal is continuously added to the cupel bath or until such time as there is sufficient doré present for a full charge. During this charging period, litharge containing most of the zinc and a portion of the copper has been withdrawn from the

furnace, in order to make room for additional doré material. During this period, the arsenic and antimony content have also been removed, the greater portion being contained in the litharge.

The final stage of refining consists in removing lead, copper, bismuth, and tellurium. The copper is removed gradually, being continuously oxidized by the large amount of PbO that is present. During the latter stages of refining, the litharge is properly termed copper litharge as it may contain as much as 10 per cent copper, while so-called good litharge will contain approximately 1 to 1.5 per cent copper. Bismuth concentrates in the doré until the last stages of refining, when it becomes oxidized and is removed with the litharge. After the last litharge is removed, it is often necessary to add approximately five bars of refined lead to form additional litharge, in order to remove the last traces of impurities with the exception of tellurium. Tellurium tends to remain with the silver and is removed by successive treatments with sodium nitrate after all the litharge is removed. Fully refined doré will assay 995 parts per thousand gold plus silver, the balance being largely copper. The doré is cast into anodes for the electrolytic parting process or plates for the sulphuric acid refining process.

In instances where the doré is shipped to distant parting plants, it is cast into bars, using molds similar to those used for refined silver bars.

One man per shift is required for the operation of each cupel, and the fuel varies directly with the size of the cupel. The large cupels, having a capacity of 300,000 oz. doré, will require 270 gal. of oil per day, the cycle on the larger cupels being 3½ days.

PART II. TREATMENT OF ELECTROLYTIC SLIMES

By Donald M. Liddell[1]

Treatment of Copper Slime.—The slime produced in the electrolytic refining of copper varies in both quantity and composition with the kind and grade of anode metal refined. Most of the refineries attempt to blend and refine the pig copper in the anode-casting furnaces in order to secure anode metal assaying about 99 per cent copper. The yield of slime from this grade of anode metal should average between 1 and 2 per cent of the weight of anode dissolved. Typical examples of copper anode slime are given in the following table:

	1	2	3	4	5	6	7
Ag, ounces per ton	6220.4	4680.5	14,012.8	9631.5	3600.0	927.90	310.5
Au, ounces per ton	143.6	64.5	91.7	96.55	800.0	402.75	10.15
Cu, per cent	18.24	28.09	13.53	4.47	40.0	69.03	46.53
Ni, per cent	1.63	2.64	0.54	0.27	......	2.03	23.13
As, per cent	0.32	1.12	2.16	1.97	......	0.15	0.28
Sb, per cent	4.56	3.54	3.04	7.20	......	0.15	0.68
Bi, per cent	Trace	None	Trace				
Se, per cent	18.05	16.14	4.27	1.15	22.0	0.85	6.60
Te, per cent	2.36	2.21	1.07	0.85	3.7	1.50	0.27
Pb, per cent	4.95	1.93	8.83	25.34	......	0.79	1.53
Zn, per cent	Trace	Trace					
S, per cent	3.31	4.09	5.31	4.99	......	15.41	1.58
Fe, per cent	0.41	0.53	0.38	0.25	......	1.04	0.41
SiO_2, per cent	4.27	6.35	....	0.43	......	0.41	0.93
Sn, per cent	1.05	0.23	....	0.15	......	0.09	0.31

[1] This section is a major revision of the contribution by W. C. Smith in the original edition.

Samples 1 to 4 were composite samples of the slime from at least 10,000 tons of anodes. Sample 5 is in the main a slime derived from Noranda bullion. Sample 6 was taken from a run made on low-silver, high-gold anodes; sample 7 was taken from a run on high-nickel anodes.

Slimes-treatment processes,[1] to be successful, must fulfil several requirements which may be listed as follows: minimum metal loss; prompt delivery of the bulk of the gold and silver; delivery of the by-products in a recoverable form; economy of operation; and the introduction of no chemicals to the process which may have an injurious effect on the refining of copper if they later enter the electrolytic circuit.

In the early days of electrolytic refining, the slime was screened to remove metallic copper, washed to free it of soluble copper salts, filtered to remove excess water, and cupeled with lead in a cupel furnace. The lead loss was heavy, and the litharge was fouled with copper. It was discovered that much better results were obtained in the furnace work with a slime from which the copper had been removed.

Copper Removal.—The first method employed for the removal of the copper from screened raw slime was to boil the slime with dilute sulphuric acid to which sodium nitrate was added in small doses. The boiling operations were conducted in lead-lined tanks equipped with paddle or air agitators; the slime was run into the tank, and enough sulphuric acid was added to make a 50 per cent sulphuric acid solution; the mixture was then heated with steam to the boiling point, and the sodium nitrate was added a few pounds at a time. Heavy fumes of poisonous nitrous gases were given off, and if the sodium nitrate was added in too large doses, the charge would foam over the top of the boiling tank. It often required 48 to 72 hr. to reduce the copper in the treated slime to 2 to 3 per cent. The lead tank lining was rapidly attacked and needed frequent repairs. The copper solution from the slime leaching was settled to remove the last traces of suspended slime and added to the tank-house electrolyte. So long as the electrolyte purification system withdrew a large volume of solution for the manufacture of copper sulphate, no trouble from sodium compounds in the electrolyte was experienced, but with the decreased market for copper sulphate and the cyclic purification methods later developed for electrolyte treatment, the sodium salts accumulated in the electrolyte and caused trouble.

The raw slime was also treated for the removal of copper by boiling with 50 per cent sulphuric acid to which manganese dioxide was added in small quantities at a time, until the copper had been oxidized and dissolved. The addition of an excessive amount of the manganese dioxide at one time would cause the charge to foam over the top of the boiling tank. The copper solution from the boiling of the slime contained manganese sulphate, and this solution could not be added to the regular electrolyte as the manganese salt caused trouble in the electrolytic cells. The solution was, therefore, sent to the copper-sulphate plant and was used for the production of bluestone. The manganese salts eventually went to waste in the spent liquors from the iron cementation tanks in which the last of the copper was precipitated from the mother liquors. These methods have been superseded by one of the several forms of either oxidizing roast or sulphatizing roast, followed by leaching with dilute sulphuric acid or water.

Oxidizing Roast.—When screened raw slime is subjected to an oxidizing roast, most of the copper is rendered soluble in dilute sulphuric acid.[2] This is due to the conversion of the copper and cuprous oxide into cupric oxide. The greater part of the copper in some slimes is rendered soluble at as low a temperature as 140°C. However, a temperature of 400 to 500°C. is required with most of them to render 95 per

[1] ADDICKS, "Copper Refining," p. 107.

[2] However, it seems preferable to use the sulphatizing roast rather than a plain oxidation, as this also eliminates much of the selenium.

cent of the copper soluble. Roasting at the higher temperatures usually also renders some of the silver and selenium acid-soluble. The details of roasting experiments on slimes 6 and 7 of the table on page 220 are as follows:

Sample	Roast, 6 hr. at, °C.	Per cent acid-soluble Cu	Soluble Ag	Soluble Se
Slime 6	140	12.34	No	No
	250	71.96	No	No
	400	91.96	No	No
	500	96.53	Yes	No
Slime 7	200	31.16 6.73 Ni	No	No
	300	67.90 10.57 Ni	No	No
	400	91.58 38.62 Ni	Yes	No
	550	99.30 11.53 Ni	Yes	Yes

Sulphatizing Roast.—Over 30 years ago, Dr. Edward Keller found that if slimes were roasted with sulphuric acid practically all the copper was converted to copper sulphate. It was his opinion that if stoichiometric proportions of acid were employed for combination with the copper optimum results were obtained. It appears, however, to be the opinion today that the best results follow with the acid in excess.

Probably the treatment of slime at Ontario East as given by C. W. Clark and A. W. Heimrod[1] and C. W. Clark and J. H. Schloen[2] represents the most modern practice that has been described.

The original slime carries 40 per cent Cu, 3600 oz. Ag per ton, 800 oz. Au per ton, 22 per cent Se, and 3.7 per cent Te. These slimes after filtering are dried at 250 to 300°F. to about 10 per cent H_2O. At this moisture there is very little dusting. They are then mixed with 75 per cent of 60° sulphuric acid and roasted at 700 to 800°F. in a Herreshoff furnace. Acid is also sprayed into the roaster during this process so that a total acid consumption of 2.2 to 2.5 lb. of acid is used for each pound of copper present.

Over 95 per cent of the copper is rendered soluble by this means, and the use of this excess of acid causes the volatilization of 80 to 95 per cent of the selenium present which is caught in the fume-collecting system attached to the roasting furnace. The collected fume furnishes the basis for the plant's selenium recovery. The slime after leaching with the copper carries about 4 per cent Cu, 11,700 oz. Ag per ton, 26 oz. Au per ton, 15 per cent Se, 11 per cent Te. If the copper-sulphate solution shows silver, it is precipitated with a little copper scale. The solution after removal of silver is electrolyzed to produce copper and sulphuric acid, the acid being used in the treatment of future slime.

After removal of the copper, the slimes are leached with caustic-soda solution which removes the tellurium by washing, as sodium tellurite, which is used as a source of tellurium. The filtered and washed slimes contain about 4 per cent Cu; 12,000 oz. Ag per ton, 2700 oz. Au per ton, 14 per cent Se, 1.5 per cent Te.

These slimes are smelted with soda and fine silica in a doré reverberatory furnace with magnesite lining. The first slag contains most of the lead, arsenic, antimony, and iron and goes back to the anode furnace. The charge is then blown with air with fused soda ash for flux to eliminate the tellurium. This second slag is leached with the caustic liquor from the slimes treatment, which takes out the selenium and tellurium, the leached slag going to the anode furnace.

[1] *Trans. Electrochem. Soc.*, Vol. 61, 1932.

[2] *A.I.M.E., Tech. Paper* 982, Class D 57, 1938.

The doré in the furnace is given a final refining with niter to remove the copper, this slag going back also to the anode furnace.

Furnace Refining of the Treated Slime.—The first refineries treated the boiled and leached slime with lead in cupel furnaces, and this method is used today at those plants which refine both lead and copper. One method for charging the slime to the cupel furnace consisted in packing the slime in small paper bags which held 15 to 25 lb. of slime and in charging the bags of slime onto the surface of the molten lead in the furnace. This method probably caused a heavy dusting loss. A better method consists in mixing the slime with litharge and a little fine coal and smelting the mixture in a small basic-lined reverberatory furnace to a slag and metal. The metal is cast in the form of bars and is fed to the cupel as needed; the slag is smelted in the lead blast furnace. Most of the copper refineries are not operated in conjunction with a lead refinery; hence other methods of treatment were developed.

The melting of treated slime in a basic-lined reverberatory furnace yields a lead-antimony slag, called tapped or sharp slag, and a metal that consists of Ag, Au, Se, Te, some Cu, and other metals. If the slime carries considerable selenium or tellurium, a third product, a matte or speiss, in which selenium and tellurium take the place of sulphur, may be formed. This matte or speiss is a most troublesome material to handle and may carry as much as 50 per cent silver. Several methods are used either to prevent the formation of this matte, or to decompose it after it has been formed.

Fluxing the Slime.—The treated slime is often mixed with fluxes before charging to the melting furnace. The fluxes used are silica, lime, soda ash, salt cake, niter cake, caustic soda, or a mixture of several of these. The thin slag that is formed is tapped from the furnace, and the metal is oxidized by forcing compressed air under the surface of the metal through iron pipes. A second slag is formed, which is skimmed off, and the metal is refined to doré with air and niter, or niter and soda ash. When slimes carrying excessive amounts of copper, selenium, and tellurium are being furnaced, a matte will separate from the metal during the refining process; this matte retards the refining operations and is best handled by tapping off, crushing to 10 mesh, roasting and leaching with sulphuric acid for the removal of the copper before returning to the melting furnace.

The following data[1] show the composition of the matte at different stages during an attempt to oxidize it in the melting furnace by means of air, niter, and soda ash Samples were taken every 4 hr. over a period of 28 hr.

Sample No.	Au, ounces per ton	Ag, ounces per ton	Cu, per cent	Se, per cent	Te, per cent
1	139.15	13,751.8	20.67	22.83	0.50
2	105.55	14,336.0	22.88	20.80	1.20
3	67.42	14,139.3	25.33	19.34	1.35
4	25.70	12,016.0	33.07	15.25	1.52
5	18.15	9,685.1	33.81	12.05	2.48
6	10.20	8,707.9	31.83	7.67	2.44
7	6.85	8,102.5	47.32	0.62	1.20
8	5.10	7,664.9	49.40	0.15	0.07

[1] Personal notes of W. C. Smith.

These slimes had been given an oxidizing roast only, and the difficulty of eliminating the selenium shows the advisability of the sulphatizing roast.

At one plant, the treated slime is melted without flux to a sharp slag and a matte or speiss and metal in one furnace; the slag is tapped off, and the metal and speiss are transferred to a second furnace in which the mixture is refined to doré with air, caustic soda, and niter.

The sharp slag from the slime-melting furnace usually carries 0.5 to 4 oz. per ton of gold; 125 to 500 oz. per ton of silver; with varying amounts of copper, lead, and antimony. A typical slag will assay about as follows:

Oz. per ton		Per cent							
Au	Ag	Cu	Pb	Ni	As	Sb	Se	Te	SiO_2
0.80	458	3.99	16.76	0.27	0.97	5.18	0.58	0.52	18.0

The sharp slag is sold to the lead smelter for the gold, silver, and lead contained in it; is smelted to copper matte in the ore-smelting furnaces and the matte blown to blister copper in converters; charged to the anode furnaces; or smelted to black copper in the copper blast furnace. The last two methods are the least desirable, since the sharp slag contains many impurities which go into the anode or the black copper and are circulated through the process. A partial elimination of these impurities is made in both the matte smelting and converting operations; hence this method of treatment gives a better elimination of the impurities, but, unfortunately, many of the refineries do not smelt sulphide ores.

Sharp slags, which contain high silver values, and the second slags, produced during the refining stage, are generally re-treated in the slime-melting furnaces either with slime or in separate campaigns, and eventually report as sharp slag.

The soda-niter slags are either charged to the slime-melting furnaces with slime, or are first crushed and leached for the removal of the selenium and tellurium contained in the slime, and the leached residue is returned to the slime furnace.

Slime Furnaces.—Small oil-fired reverberatory furnaces lined with magnesite or chrome brick are used for the melting of the slime. The charge is introduced at intervals, and each batch is melted down before the next charge is made. Sharp slag is often tapped from the furnace several times before the furnace is fully charged. It is customary to add a small amount of coal to the slag, ½ to 1 hr. before the slag is tapped, in order to secure a cleaner slag. The slime may be charged to the furnace through the regular working door by shoveling, or by dropping from hoppers through charge holes in the furnace roof. The life of a furnace bottom is 6 to 12 months; the side walls and roof require patching about every 30 to 60 days.

Metal absorption of a furnace is almost directly proportional to the volume of the brickwork below the metal line of the furnace; hence, in order to reduce the interest on the metals tied up in furnace linings, the furnace should be of such design as to have the maximum capacity with the minimum of lining consistent with good fuel consumption and furnace life. A thinly lined cylindrical tilting furnace has been developed. Two small furnaces of this construction replaced one furnace of the stationary type; each furnace melts and refines a charge of 6 to 8 tons of slime in 48 to 60 hr., while the larger furnace requires 90 to 120 hr. to treat 12 to 15 tons of slime. The two small furnaces absorb less metal than the single larger furnace and also make

an interest saving of 5 to 6 days on the metals in process. This saving is made by the reduced time the slime is waiting for furnace treatment, the reduced time the metal is in the furnace, and the reduced time the doré is awaiting parting because of the delivery of very large batches to the parting plant necessary with the large furnace.

Metal Losses.—The gases from the slime-roasting, -melting, and -refining furnaces contain Ag, Au, As, Sb, Se, and Te; hence some method for the recovery of the values from the furnace gases is necessary. The losses are due to both volatilization and mechanical dusting of the charge. As much as 1.25 per cent of the silver in the slime treated has been recovered from the furnace gases. The earlier plants used settling chambers and water scrubbers, but these were never satisfactory. Baghouses could not be used because the acid in the gases rapidly destroyed the bags. Cottrell precipitators are used for this work with good results. The treaters may handle the gases either hot, or wet and cold. The hot treater can be made of steel, but the wet treater must be constructed of lead or other acidproof material. The wet treaters are more expensive to build than the hot treaters, but have found the most favor.

There seems to be no question that silver refineries should be equipped with both scrubbers and Cottrell precipitators. The very modern plant at Ontario East has a brick flue followed by a steel flue in which the gases cool to about 400°F. and from which they enter three tower scrubbers that are fitted with sprays and rain plates. About 90 per cent of the material that passes the flues is recovered in these scrubbers. The gases leave the scrubbers at about 125°F. and go to Cottrell tube precipitators 12 ft. long. A constant watch is kept on the effluent gases from the Cottrell, but the loss is said to be less than $2 a day. Both the scrubber system and the Cottrell use antimonial lead to resist the highly corrosive gases. The scrubber solution goes to the selenium precipitating plant, while the scrubber mud goes back to the slimes-roasting furnace.

Recovery of By-products.—The by-products of greatest commercial importance in copper slime are selenium, platinum, and palladium. The platinum and palladium remain with the gold and silver, are delivered to the parting plant in the doré, and are recovered during the refining of the gold. Reference should be made to the separate chapters covering these metals.

Wet Methods for Slime Treatment.—Much thought and money have been expended in trying to develop wet methods for the treatment of slime, and several promising schemes have been given large-scale tests, but no such methods are in use at the present time. The wet treatment of the slime for the removal of the copper, followed by furnace refining to doré and the parting of the doré, is far from perfect, but yields better results than any wet process known. The methods used for the treatment of the lead slime produced by the Betts process of lead refining are given on page 378, Electrolytic Refining of Lead, and pages 141 to 142, Bismuth.

Treatment of Electrolytic Tin Slime.—The American Smelting & Refining Co., at the Perth Amboy, N. J., plant, at one time operated an electrolytic tin refinery. Very little information relative to the process has been given out. It is known that the impure tin treated carries lead, bismuth, and silver as the chief impurities. The slime is said to have carried Sn, 30; Pb, 20; Bi, 20; Cu, 5; As, 3; Sb, 5; and it is said over half the lead was present as sulphate. No details of its treatment were given out, nor has the author ever been able to ascertain the precious-metal content. If the slime were to be charged to the cupel furnaces the tin would be lost.

OTHER SILVER- AND GOLD-BEARING MATERIALS

Treatment of Cyanide Bullion.—The silver bullion produced by the cyanide treatment of silver and silver-gold ores is often refined and parted at the large refineries

on a custom basis. The bullion is weighed and sampled, either by drill sampling or by melting and dip sampling, charged to the cupel furnaces or the slime-refining furnaces, and refined to a suitable doré for parting.

The cyanide precipitates at Pachuca, Mexico, are first treated with dilute sulphuric acid to remove as much zinc as possible; are then melted in a basic-lined reverberatory furnace; and are refined with air to a very high-grade doré for electrolytic parting. Low-grade cyanide precipitates are treated at some of the lead refineries by mixing with litharge and a small percentage of coal, and smelting to a rich lead, which is then treated in the cupel furnaces.

Sulphide precipitates are handled in the same manner, except that no coal is used in the mixture; the sulphur in the precipitates reduces sufficient litharge to metallic lead to collect the values. The litharge slags from this furnace are re-treated in the lead blast furnace.

Jewelry Sweeps and Other Industrial Wastes.—These materials are usually in a very finely divided state when received, and are sampled and graded into two classes according to the assay value. High-grade material is often charged directly to the cupel or slime furnace in order to get the bulk of the precious metals on the market as soon as possible. The low-grade materials are sintered, briquetted, or nodulized with other fine material and smelted in either lead or copper blast furnaces. The lead bullion or copper matte, or both, serve as the collector for the precious metals, and these products are treated for the precious metals they contain. The rich lead is either desilverized by the Parkes process or, if sufficiently rich, is sent to the cupels directly. The copper matte is blown to blister copper in converters and refined electrolytically; or the converter copper is shotted by pouring in a thin stream into water; the shot copper is dissolved in shot towers or oxidizers by sulphuric acid; the copper is crystallized as blue stone, and the insoluble residue from the shot copper is treated in the cupel or slime furnace for the values contained in the copper.

A general rule not always observed in the treatment of very rich material is that it is often wise to make chemical perfection subservient to saving interest charges on the metals tied up in the process.

CHAPTER IX

THE METALLURGY OF COPPER

By Francis R. Pyne[1]

The ores of copper may be classified under three main groups: native copper ores, oxide ores, sulphide ores. Native copper ores occur principally in the northern part of Michigan, and in three main forms: vein deposits, in which the copper occurs at times in enormous masses; amygdaloidal diabase, through which copper is disseminated; conglomerate, in which the cementing material consists, to a degree, of metallic copper. Native copper also occurs in China to a small extent. In Chile it occurs as copper barilla, in which the fine metallic particles are disseminated throughout sandstone.

The principal oxide ores are malachite, $CuCO_3.Cu(OH)_2$; azurite, $2CuCO_3.(CuOH)_2$; cuprite, Cu_2O; atacamite, $CuCl_2$; and brochantite, $CuSO_4.3Cu(OH)_2$. The oxide ores form much of the bulk of the South American and African copper supply. The principal sulphide ores are chalcocite, Cu_2S; chalcopyrite, $Cu_2SFe_2S_3$; covellite, CuS; bornite, $3Cu_2SFe_2S_3$; and to these should be added copper-bearing pyrite, FeS_2.

The sulphide ores, however, furnish the bulk of the copper supply of the world, though the oxide ores are of importance. The advent of the flotation process of concentration followed by the development of selective flotation has virtually eliminated the direct smelting of ores and has substituted, therefor, the high-grade concentrate resulting from the practice of flotation concentration prior to smelting.

Smelting of Sulphide Ores.—In the smelting of sulphide ores, which may be considered as mixtures of copper and iron sulphides accompanied by siliceous or basic gangue, advantage is taken of the strong affinity of copper for sulphur and its weak affinity for oxygen, in comparison with the other bases in the ore. The object of smelting is to cause by fusion the conversion of the gangue into as valueless a slag as possible by the addition of proper fluxes, and at the same time to concentrate the copper and other valuable constituents of the ore into a small amount of high-grade material for further treatment.

Two important materials are formed during the smelting of copper-sulphide ores: (1) the slag produced by the combination of the gangue of the ore and the added flux; (2) the matte which is the product of the fusion of the metallic sulphides. Of these two products, the slag receives the first consideration of the metallurgist, because the sulphides melt readily under almost any circumstances, but unless the slag-forming constituents are properly proportioned serious difficulties will result.

A satisfactory slag must possess the following qualifications: (1) It must be as economical as possible, and to this end the other qualifications are subordinated, as a scientifically perfect slag may in the end be so expensive that any margin of profit is wiped out in its cost. (2) It must be sufficiently liquid to flow freely, but should not require an excessive amount of fuel to produce this condition. (3) The specific gravity should be sufficiently below that of the matte to permit the latter to separate thoroughly from it.

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The type of slag to be made depends, of course, on the slag-forming constituents available, and on the following general properties of the silicates.

Subsilicates.—While these slags are very fluid, they have a high formation temperature, and the specific gravity is so high as to make clean settling difficult, thus causing high metal losses. In addition, they are very corrosive and destructive to furnace and settler linings. Their formula is $(FeO)_2.SiO_2$.

Monosilicates.—These are quite fluid, but have a high formation temperature and are of sufficiently high specific gravity to make clean settling difficult. Basic silicates have a high dissolving power for metallic sulphides and thus tend to increase the metal loss in the slag.

Sesquisilicates.—These are mixtures of monosilicates and bisilicates, and are generally employed in smelting operations. They are sufficiently fluid to flow freely, the formation temperature is not excessive, and the specific gravity is sufficiently low to permit of clean settling with a consequent reduction of the metal loss.

Bisilicates.—These slags have a lower formation temperature, and the specific gravity is low. But they are more or less thick and viscous unless a high working temperature is carried in the furnace, so that the slag flows freely. Consequently, they require more fuel and thus are more expensive. When used they are, however, very clean slags. Their formula is $FeO.SiO_2$.

Trisilicates.—These are seldom met with in any metallurgical practice as they require a very high temperature for their formation, and, as they are extremely viscous, require an excessive amount of fuel in order that they may flow properly.

As silicates with two or more bases are characterized by increased fusibility and fluidity, up to a certain point, it frequently becomes advantageous to have a small percentage of lime present. Frequently, on account of a shortage of iron, it becomes necessary to replace it with lime to a considerable extent, and this generally adds to the cost of the slag.

The amount of matte formed is dependent on the amount of available sulphur in the ore. By available sulphur is meant that sulphur that is present when the temperature of the furnace is such that chemical activity commences between the copper, iron, and sulphur.

When the raw sulphides are subjected to heating in a neutral atmosphere, any sulphur in combination with copper in excess of the compound Cu_2S will be expelled, and the product of fusion will be Cu_2S, which may be said to be the stable compound of copper and sulphur. Similarly with the iron sulphides, any sulphur in combination with iron in excess of the compound FeS will be expelled, and a fusion will result in the formation of this compound. Should, however, the heating be carried to a point somewhere between 1200 and 1500°C., a further amount of the sulphur is volatilized and an equivalent amount of metallic iron is set free, giving a compound that may be written FeFeS, which is of great importance in pyritic smelting.

From the above it is seen that chalcopyrite, $Cu_2SFe_2S_3$, will lose about one-quarter of its sulphur by heat alone; covellite, CuS, will lose half of its sulphur; bornite, $3Cu_2SFe_2S_3$, will lose one-sixth of its sulphur, and pyrite, FeS_2, half its sulphur. For all practical purposes, matte may be considered to be a mixture of Cu_2S and FeS in varying proportions. It is also an excellent collector of gold, silver, and the other precious metals.

An ore high in sulphur and iron, but low in copper, will, upon fusion, produce a matte containing so low a percentage of copper that its subsequent treatment would, under ordinary circumstances, cost too much, and as it is the object of the metallurgist to concentrate the copper in his products up to the most economical point, steps must be taken to reduce the amount of sulphur available for the formation of matte and lower the amount of the latter produced per ton of ore smelted.

Such reduction may be accomplished in two ways, by an oxidizing roasting, or by subjecting the ore to an oxidizing fusion. When the ore occurs as massive sulphides, the latter method is frequently used where conditions make it economical; when the ores are not massive, the oxidizing roast is the predominating method.

Roasting is the heating to an elevated temperature, without fusion, or at least only with incipient fusion, of ores or metallic compounds in contact with oxidizing materials, in order to produce a chemical change or to eliminate a component by volatilization. In copper metallurgy, the oxidizing material is the oxygen of the air, and the object is the partial elimination of the sulphur in the ore.

When a metallic sulphide is heated to a sufficiently high temperature with access of air, sulphur dioxide is formed together with a metallic oxide.

$$2MS + 3O_2 = 2MO + 2SO_2$$

Proper oxidation requires a temperature sufficiently high to produce the necessary affinity between the oxygen and the sulphur, but it must not be so high as to cause the surface of the ore particles to melt and form a protecting layer which retards the oxidizing action and may even cause it to cease. This temperature may be obtained by the combustion of extraneous fuel or by the heat of oxidation of the constituents of the charge.

A second requirement for proper oxidation is a constant and abundant supply of air in immediate contact with the surface to be oxidized. The necessity for an abundant supply is due to the fact that the oxidizing power of the air is lowered out of all proportion when diluted by the products of oxidation. In other words, if the air for oxidation is diluted with its own volume of gaseous products, the oxidizing effect of the resulting mixture will be much less than half the oxidizing power of pure air. The more rapidly the gaseous products are removed and replaced by pure air, therefore, the more rapid will be the roast.

The speed and the thoroughness of the roast are also governed by the size of the particles in the roaster. It is obvious that the finer the ore is crushed, the greater will be the surface exposed to the oxidizing influences. However, as fine material always results in losses through handling, flue-dust losses, etc., it will be seen that there is an economical point where the increased speed of roasting will be offset by the losses in material, the recovery of which necessitates expensive installations. The usual charge to a roaster consists of a mixture of relatively coarse and fine particles, and the roast is carried to a point where the overroasting of the fine particles balances the underroasting of the coarse particles, so that the final mixture from the roaster gives the desired sulphur content. The various types of apparatus used in roasting copper ores may be roughly classified as follows: heaps, stalls, cylindrical furnaces with superimposed hearths, blast-roasting apparatus. These methods will be found described at length in Chap. X of the first volume, "Principles and Processes."

Types of Smelting Furnaces.—Flotation concentrates constitute the major portion of the modern smelter's intake. Such concentrates consist of finely divided particles and range from 20 per cent copper upward to 30 or even 35 per cent. As a consequence, the blast furnace has become relatively obsolete, being almost universally supplanted by the reverberatory furnace.

The blast furnace is used mainly for the treatment of coarse ores over 1 in. in diameter, though in many cases much finer ore than this is treated successfully; however, the development of the modern reverberatory has progressed to the point where it has often been found to be more economical to crush the coarser ore to ¼ in. and treat in the reverberatory rather than in the blast furnace.

The early types of blast furnace were constructed of brick, and the molten products were collected in a crucible located at the lowest point of the furnace. This type of

furnace had two great disadvantages in addition to its small capacity. These were the destruction of the shaft at the smelting zone, and the impossibility of making a clean separation between the slag and the matte.

The first of these difficulties was overcome by the adoption of the water jacket, which not only eliminated the corrosion, but also permitted a higher temperature to be carried, resulting in a more fluid slag. The second difficulty was solved by the use of the external settler, which not only gave an efficient separation between the slag and matte, but also allowed the speed of the furnace to be greatly increased.

The modern blast furnace consists essentially of a long, narrow, water-jacketed shaft. The dimensions, particularly the length, vary considerably, being proportioned to the capacity of the furnace. The size of furnaces is expressed in terms of the dimensions at the tuyère level. The width, being limited by the ability of the blast to penetrate the charge, is generally 44 to 48 in., though some furnaces are as narrow as 30 in., and others as wide as 56 in. As the width is practically fixed within narrow limits, the only manner in which capacity may be obtained is by increasing the length, and present-day furnaces have lengths of 180 in. to as much as 1044 in., in the case of the huge Anaconda furnaces. The capacity of blast furnaces depends greatly upon local conditions but may be said to vary from 4.5 to 9.0 tons per sq. ft. of hearth area per day. The bottom plate of the furnace is generally a heavy ribbed cast-iron plate, supported by jackscrews. Upon this is laid a layer of fire-brick, though special circumstances may require the use of silica or chrome brick. Resting on the bottom plate are heavy cast-iron plates bolted together, forming the walls of the crucible. These are generally heavily ribbed to ensure the necessary strength and are lined with the same material as is used on the bottom. In some instances, the walls of the crucible are formed by a set of water jackets, but the usual practice is to have the lower tier of water jackets rest directly upon the bottom plate, the lower ends being below the level of the matte and slag to prevent their burning through in case sediment collects in the water space.

When the blast furnace is started, the radiation from the bottom and through the water jackets forms a crust of chilled material which remains permanently. This crust adjusts itself to the operations of the furnace. If it wears down, the increased radiation soon restores it to the proper thickness, while if the furnace cools down the radiation is decreased, the bottom builds up, but when the furnace is once more at proper heat, the additional thickness is soon melted off.

The water jackets are generally in two tiers. The lower jackets rest either on the crucible plates, or, as has been stated, directly on the bottom plate. The upper tiers are suspended from I beams which carry the furnace superstructure. The upper jackets rest on the top of the lower jackets. The lower side jackets are given a slope toward each other to form a bosh, the upper and end jackets being vertical. The amount of bosh depends on the amount of reducing action desired, as the greater the amount of bosh, the greater will be the reducing action. The water jackets are constructed of flanged steel plate, the inner side being 5/16 to 3/8 in. thick, the outer side being somewhat thinner, 1/4 to 5/16 in. The water space between the sides of the jacket varies from 3 to 5 in. The jackets are stiffened by means of angle iron running vertically in the water space. Each jacket has its individual feed and discharge pipes for the cooling water, and where water is plentiful each jacket may be on a separate circulation, but where water is scarce the outlet of the lower jackets may be fed to the upper jackets.

The lower side jackets are pierced for the tuyère openings, there being usually three tuyères to each jacket. The opening is usually 4 to 6 in., and a steel thimble having a slight taper is welded to the inner plate and riveted to the outer plate. The tuyère pipes are generally of cast iron, and are bolted securely against the jackets, any leak-

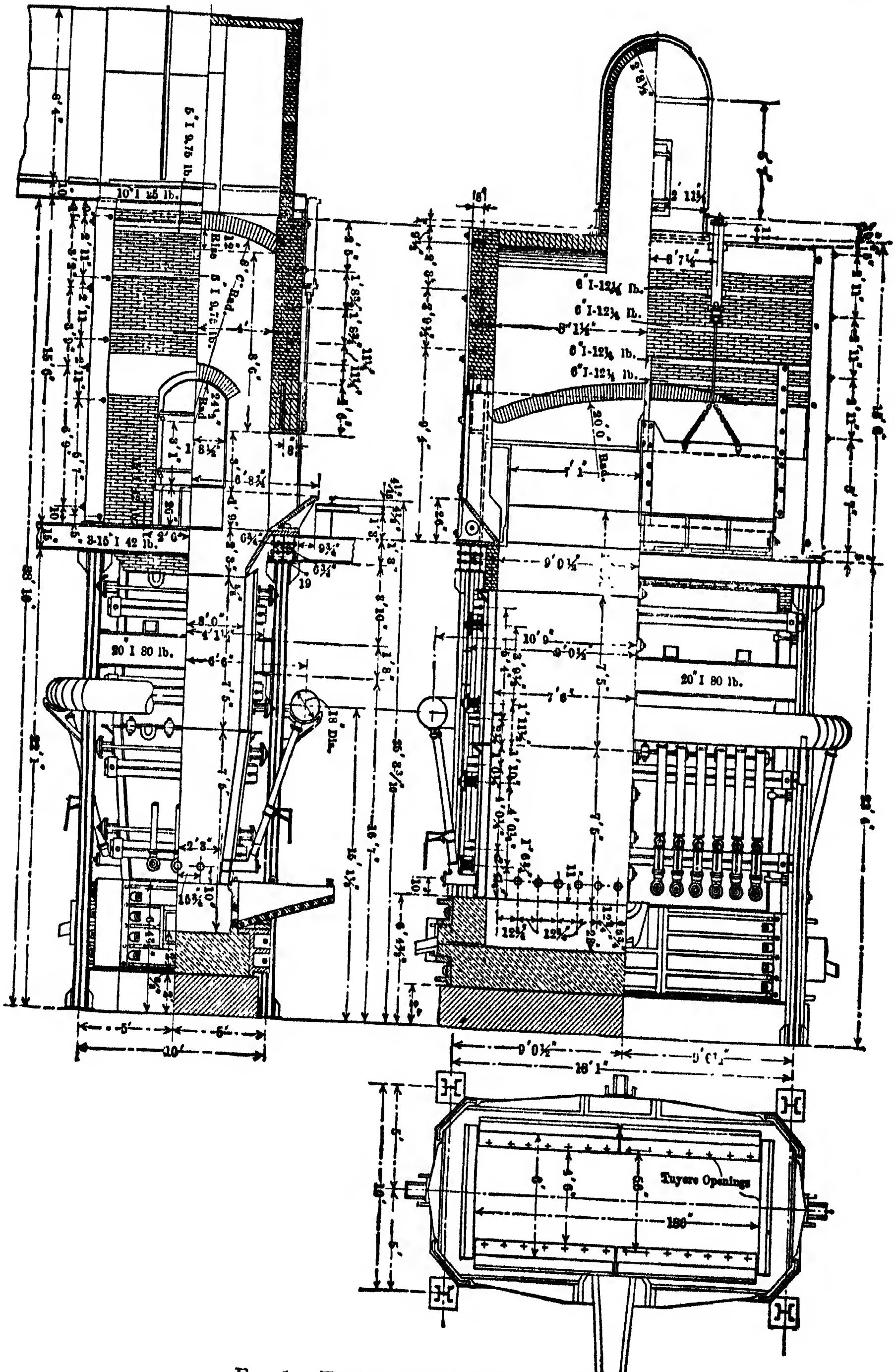


FIG. 1.—Typical copper blast furnace.

age being prevented by asbestos packing. There is usually a cap on the outer end of each tuyère pipe, which is readily removable to permit of punching the tuyères when necessary.

The tuyère pipes are connected by short branches to the main bustle pipe which carries the main air supply, the amount of blast to each tuyère being regulated by means of a valve. The volume of air required by the furnace varies widely, published figures being 190 to 400 cu. ft. per min. per sq. ft. of hearth area at a pressure of 32 to 40 oz. It is probable that the variation in these figures is due to their being derived by taking the revolutions per minute of the blowers or the piston displacement, neither of which is accurate, owing to the great amount of leakage.

The breast jacket is located either in the side or the end of the furnace, the location being largely determined by the available floor space and the general arrangement of the plant. It contains the opening for the removal of the molten products of the furnace and is securely attached to the adjoining jackets. The slag spout conveying the slag and matte from the furnace to the settler is fastened to the breast jacket in such a manner as to permit of its ready removal when required with minimum delay to the furnace operations. The spout may be constructed of wrought iron, steel, copper, or bronze, and is water-cooled. The blast is trapped by having the discharge end of the spout about 18 in. above the opening in the breast jacket, so that as the molten material from the furnace rises in the spout there is sufficient head to overcome the pressure of the blast. The shape of the slag spout depends upon the fancies of the designer of the furnace, there being many different designs in use, all of which appear to be giving satisfaction.

The jackets generally carry the shaft of the furnace to the level of the charging floor, though in some instances they are surmounted by several courses of firebrick. Just below the charging floor there is generally a set of feed or apron plates for the purpose of distributing the charge uniformly in the furnace by directing the fine material toward the center of the shaft while permitting the coarse material to fall along the sides. In many furnaces, however, these plates are omitted owing to local conditions making their use unnecessary.

Above the level of the charging floor is the superstructure of the furnace with the arrangements for feeding the materials of the charge and the removal of the furnace gases. There are many modifications in the design of the superstructure. In many cases it is of brick to a height of 12 to 14 ft. surmounted by a steel hood for the removal of the gases. In other plants the entire superstructure is of steel and occasionally water-jacketed.

The general practice of charging is through openings in the sides of the superstructure, which may or may not be kept closed by doors between charging. With the development of mechanical charging devices the gases are in some instances drawn off below the point of charging, particularly where the gases are utilized in the manufacture of acid. Care should be taken to keep the charge openings closed between charges on account of the great leakage of air that would otherwise occur, with its consequent detrimental effect on the draft of the furnace.

Air- or water-cooled steel hoods have marked advantages over the brick hood on account of the ready removal of accretions therefrom, and there seems to be less tendency for these accretions to form on this type of hood.

The furnace gases, on leaving the hood, pass through a downcomer of brick or steel, then to some sort of a settling chamber to remove the coarse particles of dust, and thence to the stack. The recovery of the flue dust is a matter of serious importance, and the methods used will be discussed at a later point.

The settler serves not only as a means for separating the slag and matte by reason of the difference in their specific gravities, but also as a reservoir for the storage

of matte until such time as it may be required. A plant that treats its own matte, therefore, requires a larger settler than does one that casts its matte directly into molds for shipment to some other plant for treatment. The settler is circular or oval, depending on local conditions and the plant layout, and consists of an iron shell lined with refractory material. The diameter may be as great as 26 ft., though 18 ft. is the usual dimension, the depth being 4 to 5 ft. The lining material varies greatly and depends on the grade of the matte, and character of the slag, the most rapid wear being occasioned by the very corrosive and fiery low-grade mattes usually accompanied by basic slags. A high-grade matte and an acid slag seldom cause much trouble through corrosion. The settler lining, where there is little corrosion, may be made of firebrick or silica brick; where corrosion is feared, the lining is generally of magnesite or chrome brick, or a combination of the two. Frequently, chromite or chrome ore is rammed into place and faced with a row of bricks to hold it in place until the heat of the molten material sinters it together. The lining is frequently protected by spraying water on the steel shell of the settler; this keeps the outside cool and causes a crust to form on the lining.

The roof of the settler is formed by the chilling of the slag, amounting to a thickness of several inches except at the point where the molten stream enters and leaves. The working platform was formerly this chilled crust but is at the present time a steel platform directly over the settler.

The slag overflows are constructed of cast iron coated with clay or other material, and are situated as far away from the entrance as possible, thus affording more time for settling. In many cases these overflows are situated at the side of the settler, due to the arrangement of the plant. The slag quietly flows out of the settler, and through these overflows into slag cars by which it is conveyed to the dump, or else it may be granulated by means of a strong stream of water, which not only granulates it but also carries it through launders to the dump.

The matte is withdrawn from the settler through tapholes situated close to the bottom. There are generally two of these holes, though many plants have but one. The hole in the wall of the settler is 1½ to 2 in. in width and may be lined with chrome brick. Opposite this opening and attached to the shell of the settler is a copper or iron frame in which is securely wedged the tapping plate, which may be either iron or copper. The tapping plate has a 1-in. hole in the center into which a clay plug is rammed. A steel tapping bar is rammed through the clay plug until it almost reaches the matte and remains in that position until the tap is made. This is accomplished by withdrawing the steel bar by sledging against wedges held in place on the bar by rings. The matte flows from the taphole into the matte launder of cast iron, thickly coated with clay to protect it from corrosion, and from there into the ladle, which is usually of steel lined with cement and clay. During the tapping the workers are protected from the heat and splashes of matte by means of a slotted sheet-iron door which is swung out of the way when not required.

The charging of the blast furnace is accomplished in a number of ways. Hand charging gives the best regulation of coarse and fines and also possibly effects a saving of coke. It is frequently used up to capacities of 300 to 350 tons per day and in some cases even higher. It, however, is expensive and too slow for the average modern blast furnace smelting 600 to 700 tons per day and has, therefore, been superseded by some form of mechanical charging, particularly as the larger furnaces are less sensitive to slight irregularities in the charges than the smaller furnaces.

The general plan in use at the present time is to charge the furnace from side dump cars, varying greatly in their design, which are brought to the furnace in a train by a locomotive, and travel on tracks on each side of the superstructure. The contents of

the car may be dumped at one point, or the car may be moved along the length of the furnace while being dumped in order to distribute the charge.

Another scheme provides for the charges being brought to the furnace in cars and dumped on the charging floor from which they are pushed into the furnace by a mechanical pusher. At Granby, the furnaces were charged by pushing the charge cars into the furnace at the ends, from which they ran on tracks inside the furnace to the point of discharge. This gave a straight fall of material and provided good distribution.

In some plants the coke used for fuel is mixed with the charge and then sent to the furnace, but the usual practice is to charge it separately, and the utmost endeavor is made to keep the consumption of coke at a minimum, although this is not always easy to do, as the average furnaceman considers coke as a panacea for all ills.

Sizes of modern blast furnaces are shown in the following table:

	Area, inches	Blast, ounces	Capacity, tons
United Verde	48 by 320	40	950
United Verde Extension	48 by 312	30	600
Mason Valley	66 by 420	33	1,000
Calumet and Arizona	48 by 480	35	900
Garfield	48 by 240	40	600
Tacoma	45 by 261	35	650
Anaconda	56 by 612	40	1,400
Anaconda	56 by 1,044	40	2,500

The modern furnaces are vastly more efficient and economical than those formerly in use. Owing to the large amount of material in the furnace, they are less susceptible to slight irregularities. There is a saving of fuel, possibly amounting to 10 per cent, and there results a higher furnace temperature, giving hotter slag and enabling a more siliceous charge to be run. There is a marked decrease of incrustations, which eliminates the necessity for much barring. It has been found possible to change a leaking jacket without shutting the furnace down. This is accomplished by blocking off the tuyères in the leaking jacket as well as those in the adjacent jackets and allowing a crust to form that is sufficiently strong to support the charge during the short period necessary to make the change.

There are three distinct processes in blast-furnace smelting: (1) The reduction process, in which a considerable percentage of coke, 15 per cent, is used. The blast oxidizes the carbon of the coke and but little of the sulphur in the ore. This is the process most generally used. (2) The pyritic process, in which raw massive sulphides are smelted in a highly oxidizing atmosphere without the addition of carbonaceous fuel. The heat generated by the oxidation of the sulphur and iron is sufficient to maintain a continuous operation. (3) The partial- or semipyritic process in which sufficient heat is not generated by the oxidation of the sulphides and carbonaceous fuel is added to the charge in just sufficient quantity to overcome the deficiency.

The Reduction Process.—This process is characterized by the use of carbonaceous fuel as the principal source of heat. The sulphur content of the charge is sufficient to form the desired matte, and any oxidation is generally undesirable.

The percentage of coke, which is the usual fuel used, varies from 12 to 15 per cent. An excessive amount of coke is liable to cause a reduction of iron from the slag, while with a shortage the furnace becomes chilled and suffers a loss of tonnage.

The use of such an amount of coke means that the furnace always contains a large mass of glowing coke for a considerable distance above the tuyères, and consequently the oxygen in the blast is consumed almost immediately, resulting in a strong reducing atmosphere. Such being the case, it is readily seen that any sulphides present will melt down unchanged and form matte. An ore high in sulphur would, therefore, yield a large amount of matte which is expensive to treat, and it is clear that little would be gained by the reducing smelting of such an ore, and that a portion of the sulphur must be eliminated by a roasting process previous to the treatment in the blast furnace, or else the sulphides may be mixed with oxide copper ores to increase the grade of the matte. A certain oxidation of sulphur may be accomplished in the blast furnace by keeping the ore column low and increasing the blast, but such procedure generally results in a very hot top and high temperatures of the waste gases and, in general, is not economical.

Regarding the chemistry of the process, the blast entering through the tuyères oxidizes the carbon of the coke to CO_2, which is then partly reduced to CO by the glowing mass of coke in the furnace, the resulting gases being a mixture of CO, CO_2, and the nitrogen of the air. As these gases rise in the furnace and reduce the oxidized materials, the percentage of CO_2 increases and will predominate in the waste gases. Any remaining CO is usually burned to CO_2 in the upper part of the furnace.

As the charge descends in the furnace, its moisture is driven off almost immediately, followed by the decomposition of such carbonates as may be present. At a lower point the oxides and silicates of copper will be reduced, and on coming into contact with metallic sulphides will be converted into copper sulphides which, with any existing sulphides, melt and flow downward to the crucible, collecting the silver and gold as they descend. Ferric oxide, Fe_2O_3, is reduced to ferrous oxide, FeO, which combines with the silica to form slag as does any lime or other flux added to the charge. When the molten materials have collected in the crucible below the tuyeres, the various sulphides adjust themselves to form the proper matte, and likewise the various slag components adjust themselves to form the proper slag.

The Pyritic Process.—The feature of this type of smelting is that the heat necessary to conduct the operation is furnished by the oxidation of the constituents of the ore, little or no extraneous fuel being used for this purpose. Up to 2 to 3 per cent of coke may be added to the charge purely as a preheating medium and possibly to secure a more open charge. It certainly never reaches the smelting zone.

The essential requirements for pyritic smelting are siliceous material which is high in free silica, and heavy pyrite ore. It is necessary for as much of the silica as possible to be in the free state in order that it may combine with the ferrous oxide at the instant of its formation. Combined silica is unsuited to the pyritic process as it is already united with one or more bases and consequently requires a large amount of heat to break up the existing combinations and form new ones with the ferrous oxide, and generally in the pyritic process there is not any too large a margin of heat.

The pyrite ore not only furnishes the heat for the operation, but also the sulphur required for the matte, and it must consist largely of iron pyrites, as any oxidation of the copper sulphides would result in the slagging and consequent loss of the copper oxides.

As the charge sinks in the furnace, any moisture present is quickly driven off, followed by the dissociation of the limestone added as flux. The free sulphur in the sulphides will be expelled as heavy fumes of elemental sulphur, and at a point just

above the smelting zone the pyrite has been changed to FeFeS, which is the true pyritic fuel of the process.

The blast entering the furnace through the tuyères strikes the hot fused sulphides, oxidizing the Fe to FeO and the S to SO_2. The FeO simultaneously unites with the silica to form a ferrous silicate slag, while the SO_2 rises through the charge and preheats it assisted by the oxidation of such coke as may be present:

$$C + SO_2 = S + CO_2$$

The matte collects below the tuyères, as does also the ferrous silicate slag after uniting with the lime to form the final slag. The fused mixture then flows through the spout to the settler.

The grade of the matte produced and the acidity of the slag are controlled by the volume of air blown into the furnace. A reduction in the amount of air will cause less of the sulphide to become oxidized, and the grade of the matte will, therefore, be lowered. At the same time the slag will become more siliceous, as less iron is oxidized, and this condition will interfere with the process unless the amount of siliceous material in the charge is reduced. On the other hand, any increase in the volume of air will oxidize an additional amount of iron, raising the grade of the matte and increasing the iron in the slag unless additional silica is provided.

A peculiarity of the pyritic process is the artificial bosh formed on the side and end walls of the furnace. This contracts the smelting area to a long, narrow slit. This bosh is composed of fragments of quartz struck together by slag or by superficial softening, and seldom contains matte. Its position in the furnace is not fixed, but varies under different conditions.

While in reducing smelting the tuyères are bright, in pyritic smelting they are dark and are bridged across. It has been stated that a bar can be passed through the furnace from one tuyère to the opposite tuyère and be cool when withdrawn. This indicates that the zone of fusion is well above the tuyère line and that the molten material passes through channels between the tuyères.

Partial pyritic smelting is used when the available sulphide ores are not massive but consist of pyritic material disseminated throughout the gangue, which is generally low in free silica and which may contain some alumina. Such ores are not capable of furnishing by themselves sufficient heat for the continuance of the process, and it is, therefore, necessary to add carbonaceous fuel. In some instances it has been found advantageous to preheat the blast, as thereby a saving is accomplished in the amount of fuel used.

In the partial pyritic process the slags are rather low in iron, as the presence of coke requires much of the oxygen of the blast for its combustion and there is less available for oxidizing the iron in the sulphides. The excess silica will, therefore, have to be taken care of by the use of lime. In order that there may be any considerable pyritic effect, a large amount of blast is necessary, and this usually results in the furnace having a hot top.

The smelting zone is nearer the tuyère level and is not so contracted as in pyritic smelting, but is higher and more contracted than in reducing smelting. The tuyères are frequently dark and require a great deal of punching to keep them open.

The principal features of the blast furnace for the treatment of coarse ores are that its construction is simple and the erection is comparatively inexpensive. Where small installations are required, they can be purchased complete and are easily transportable from one location to another. The furnace is easily started and shut down, and the operation is relatively cheap. The fuel consumption is low, and there is the possibility of utilizing the fuel value of the iron and sulphur in the charge, and the heat is efficiently communicated to the individual parts of the charge.

The blast furnace is exceedingly elastic in its operation, and changes in the ore supply are readily handled with little trouble. It is capable of handling practically every class of copper-bearing material in lump form, and, with modern sintering facilities, much fine material can also be treated that would otherwise be uneconomical to handle.

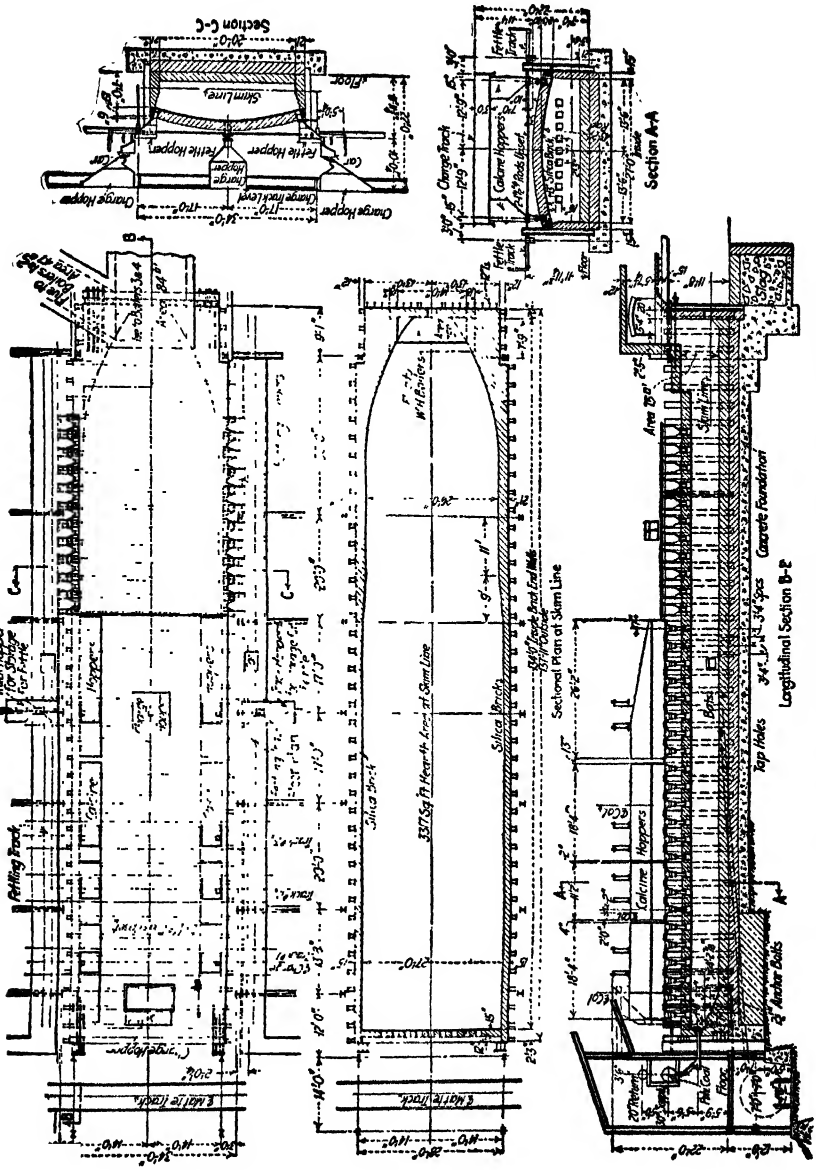


Fig. 2.—Reverberatory smelting furnace at Nevada Consolidated smelter.

The reverberatory furnace is used for the treatment of fine ores, and the fuel and ore are kept separate, the former being burned in a separate compartment from which the flame and hot gases pass over the ore, being guided in their course by a

more or less horizontal roof. The heating of the ore is accomplished by the radiation from the roof and side walls rather than by direct contact with the hot gases.

It is particularly suitable for fine materials on account of the relatively quiet atmosphere, due to there being no blast, and there are greater opportunities for the settlement of dust than in the blast furnace. As the furnace atmosphere is neutral, or very nearly so, it has little or no influence on such reactions as occur in the furnace, and it, therefore, follows that the reverberatory is purely a melting furnace.

The functions of the furnace are that it shall melt down ore and flux as rapidly as possible with a minimum of heat loss; it should permit the formation of matte and slag from the mixture of oxides, sulphides, and sulphates in the charge; and the temperature must be sufficiently high to render the matte and slag perfectly fluid in order that there may be complete settling with a minimum of loss in the slag.

In order that the furnace may melt as rapidly as possible, it is necessary that there be a good draft, in order that the great volume of gases that have been cooled down by their contact with the roof, walls, and charge be replaced as speedily as possible by fresh hot gases.

The heat losses are kept at a minimum by the elimination of side-door charging with its consequent admission of large volumes of cold air; the walls and roof are made as thick as economically possible to reduce the radiation losses.

The heat of the gases is utilized to the greatest possible extent by making the furnace as long as will permit the charge being kept in a fluid condition without an excessive consumption of fuel, and such heat as necessarily leaves the furnace as sensible heat in the waste gases is, to a large extent, recovered by passing them through waste-heat boilers.

The hearth is of silica sand 24 to 30 in. in thickness. The sand is given a preliminary calcining and is then leveled and sintered into place by long, continuous firing. As the modern practice is not to drop the charge on the hearth, but on a bath of molten material which is supported by the hearth, there is little wear on the latter, resulting in a very long life. Crushed quartz may be used instead of sand.

The reverberatories of the new Morenci plant of the Phelps Dodge Corp. are 110 ft. × 31 ft. 3 in. outside the walls, which is somewhat smaller than furnaces built some years ago, some of which were 130 ft. long. These furnaces are designed to smelt 650 tons of charge per day. The walls are stepped or tapered from 1 ft. minimum at the top to 4 or 5 ft. maximum thickness at the bottom. Construction is silica brick, lined with magnesite except in the charging zone. Silica brick is used for the arch, which is 20 in. thick, 35 ft. in radius, and is horizontal for its full length. It is 9 ft. high at the spring line, measured from the top of the silica bottom, which is at the same level as the reverberatory building floor. A 2-ft. layer of crushed silica is used for the bottom. Below this is a layer of poured slag 8 ft. thick near each end of the furnace and 4 ft. thick in the intermediate zone. The 8-ft. depth is provided in order to bury the lower tie rods for resisting endwise expansion of the furnace.

One large longitudinal tie rod runs the full length of each side of the furnace, and the buckstays are tied across with horizontal tie rods in the usual manner. Heavy concrete walls take the bottom buckstay thrust and confine the silica and slag bottom. Pilasters, 13 in. square, at the buckstays space these members from the face of the wall.

A few years ago the amount of iron sulphide in the flotation concentrates practically forced the use of roasters, and the calcines were usually delivered to the reverberatory as hot as possible. The improvement in grade of concentrates due to differential flotation is such that in the new Morenci plant roasting has entirely been dispensed with and the concentrates are charged wet through a series of charge spouts at 4-ft. centers along the furnace roof. They contain about 9 per cent moisture. Such coarse ore as is suited for direct smelting, which would formerly have been treated in

blast furnaces, is crushed to ¼ in. and added to the reverberatory charge beds. The necessary lime flux is also crushed and added to the beds.

The advantages of wet charging are the elimination of the roasting plant and the facts that there is no dusting in the furnace and that there is a great decrease in the accumulation of magnetite on the hearth. So far it has been limited to plants operating in mild climates and would probably offer great difficulties in cold climates.

Depth of the bath is nominally 3 ft. Three matte tap plates, for alternative use, are placed on each side of the furnace near the firing end, with the single slag tap in the side wall near the uptake flue. The slag launder branches to two openings over different tracks. The highly superheated bath readily gives up heat to the fresh charge, and it receives further heat from the radiation from the roof and quickly melts.

The resulting slag and matte now move toward the tapping end of the furnace and have ample time in which to separate cleanly. The slag may be tapped intermittently or allowed to flow off continuously, the latter coming more into favor as it results in cleaner slags. The matte is tapped from the fore part of the furnace, as required by the demands of the converters, in a manner similar to tapping a blast-furnace settler.

The fuel used in the modern large reverberatory furnace is gas, pulverized coal, or fuel oil, depending on the relative cheapness of the fuels. When pulverized coal is used, it is ground so that 80 to 90 per cent will pass a 200-mesh screen, and is blown into the furnace with about 15-oz. air pressure. The coal used may vary in ash content from 6 to 7 per cent up to as high as 15 to 20 per cent without giving trouble. The ratio of charge to fuel varies from 5 to 7½. The burners are inserted directly in the rear wall of the furnace and several burners are used, four to six being the usual number. The type of burner varies in each plant with apparently equally satisfactory results.

When using fuel oil in the furnaces it is generally 17 to 19 Bé and is preheated to about 200 to 250°F. before burning, as this results in fuel economy. The amount of fuel oil used per ton of charge varies from 0.50 to 0.70 bbl. When as much heat as possible has been extracted from the gases, they are passed through waste-heat boilers for a further recovery. These are 500 to 750 b.hp., and they frequently are connected to a common cross flue extending from all the reverberatory furnaces, so that in case of a shutdown of a furnace the boiler capacity will not be lost, and if a boiler is down for cleaning or repair the other boilers are available for the utilization of the waste heat. It has been found to be advisable to have the flues from the furnaces to the boilers slope slightly toward the furnaces, as otherwise trouble may be experienced from the accumulation of slag.

Natural gas is a highly efficient, clean fuel, but obviously its use is limited to localities adjacent to natural gas fields. Fuel oil and natural gas have an advantage over pulverized coal in that there is no ash which would increase the amount of slag.

In the new Morenci plant, two groups of four multiple-jet low-pressure gas burners fire through two rectangular ports. The burners are suspended from individual trolleys, permitting withdrawal from the firing position, and an oil burner accompanies each one, for emergency or auxiliary use. A suspended arch forms the top of the firing wall.

Following modern practice the 8½ × 23 ft. uptake flue is made as short as possible and branches to two waste-heat boilers. The flue bottom slopes steeply back toward the furnace to drain the slag. The roof and the back wall are of suspended construction, using magnesite brick. A solid brick damper can be dropped through a slot to cut off one boiler.

At a new Canadian plant, using suspended-arch construction, the width of the furnace is 35 ft. in the smelting zone. All Canadian plants are using side feeding, the

unsmelted charge being kept away from the skimming bay. The American Smelting and Refining Co. favors a deep-bath gun feed. Water-cooled jackets along the bath-line of deep-bath smelting furnaces appears to have become standard practice. Copper jackets with 1½-in. water coils have proved most satisfactory.[1] The use of about 3 per cent of bentonite has been found very helpful in making a silica slurry mixture that will adhere to brickwork. Magnetite sand is now (1943) being tried for reverberatory bottoms, with the hope that its higher specific gravity and lower coefficient of expansion, as compared with silica, will make it a decided improvement. The reverberatory is more independent of type slags than is the blast furnace. So far as reverberatory slags may be said to be typical, current practice appears to tend to a slag containing 37 to 38 per cent SiO_2, 39 to 40 per cent FeO, 4 to 6 per cent Al_2O_3.

In the reverberatory furnace any reducing action is performed by the sulphur in the charge. This reacts with the oxides and sulphates to produce metallic copper and sulphur dioxide. The metallic copper is then sulphurized by the sulphides of iron present, oxidizing the iron to FeO, which combines with the silica present to form the slag. The reverberatory furnace will make a higher silica slag than a blast furnace, owing to the higher available temperature. Any iron oxide, Fe_2O_3, present in the charge is acted upon by the sulphides and reduced to FeO, uniting with the silica.

The grade of matte produced by the reverberatory furnace depends upon the degree of roasting that the ore has received or the cleanness of the concentrate. If a higher grade of matte is desired, the roast is carried to a higher degree, and if the matte is too high, the roast is not pushed to the same completeness. In the roasting, care must be taken that no magnetic oxide of iron, Fe_3O_4, is formed, as such material forms a mush in the furnace and is difficult to remove. When it occurs, the remedy is to add a large amount of green sulphide ore to the charge, which will reduce the magnetite to FeO.

Comparing blast-furnace and reverberatory-furnace smelting, the former requires coarse ore in order to give the best satisfaction, little space is required, and the investment is low for any given tonnage. The fuel, though small in amount, is relatively expensive, and considerable power and a large amount of cooling water are required. Blast-furnace slags can be made between very wide limits, but the addition of a large amount of flux results in the production of a large amount of slag with a corresponding metal loss.

The reverberatory furnace is the most satisfactory and advantageous apparatus in which to treat fine ores, but it usually requires an extensive roasting plant and in itself occupies a large amount of space and locks up a large amount of valuable metal. Hence the investment is large for a given tonnage. While large amounts of low-priced fuel are used, a large proportion of the heat in the gases is recovered in waste-heat boilers and this greatly reduces the power cost. The amount of slag and, consequently, the metal loss are less than with the blast furnace. With the ever-increasing amount of fine ores to be treated, the reverberatory furnace is fast displacing the blast furnace, and it has been found advantageous in certain localities to use reverberatory smelting for coarse ores that under ordinary conditions would go to the blast furnace.

Converting.—When copper and other valuable constituents of the ore have been concentrated into the matte, and the worthless material disposed of as slag, the next step in the process is the removal by oxidation of the iron and sulphur of the matte. This is accomplished by transferring the molten matte to a refractory-lined vessel,

[1] WAGSTAFF, *Metals Tech.*, February, 1944.

known as a converter, and forcing thin streams of air through the liquid mass. The reactions involve the rapid oxidation of the iron and sulphur and the fluxing by silica of the iron oxide thus produced. The sulphur dioxide formed by these reactions passes off in the waste gases. The heat of oxidation is such that the materials are kept in a molten condition, and the temperature is maintained well above that necessary for the formation of the slag, so that the process is independent of heat from external sources. The copper, together with any silver or gold, is reduced to the metallic form and is cast into suitable shapes for transportation to the refinery for further treatment.

The converter is a cylindrical iron or steel vessel lined with refractory material. A conical mouth is provided through which the matte is introduced, the slag and blister copper withdrawn, and the gases pass to the stack. The air for the oxidation is introduced through the side of the converter by means of tuyères leading from a wind box attached to the outside and having a connection with the blast main.

The early types of converters were blown from the bottom, similar to those used in the steel industry, but this method was not a success, due to the chilling effect of the blast on the copper, which, when produced, sank to the bottom of the converter and froze in the tuyères, thus stopping the operation. This was remedied by raising the tuyères so that there was space for the copper to settle underneath the blast.

The refractory lining may be composed of either acid or basic material. The acid lining, though formerly universal, is practically entirely supplanted by the basic lining. The functions of the lining are to preserve the steel shell and form a receptacle for the molten materials, and to prevent radiation losses to the greatest possible extent.

In the acid lining the material used should contain the largest possible amount of free silica. The material generally used is low-grade siliceous ore, which, while it may not be so desirable metallurgically as quartz, is smelted for nothing, and the values recovered from an otherwise profitless material make the substitution economical. The ore is crushed and mixed with a binding material in a mill, and is pounded down hard in the bottom of the converter by tamping machines until it reaches to the proper distance below the tuyère level. At this point a steel or wooden form is placed in the converter, and the lining material is rammed around the form in layers about 6 in. in thickness. When the operation is completed, the form, which is sectional, is removed and the tuyère holes are punched in the lining. The hood is then inverted and lined and placed upon the body of the converter and securely bolted in place, the joint being covered with clay.

The freshly lined converter is now dried slowly by a wood fire, after which coke is added and kept burning by an air blast through the tuyères for 5 or 6 hr., after which the converter is ready for operation.

The basic lining is magnesite brick, the thickness varying from 9 in. at the top and sides to 18 in. along the tuyère line and bottom. The brick may be laid in magnesite powder and linseed oil, or sodium silicate may be substituted for the linseed oil. In order to furnish room for proper expansion, liners consisting of thin strips of wood are placed at intervals along the sides. After lining the shell, it is carefully warmed to prevent spalling and is then ready to be placed in the stand.

The air for oxidizing the sulphur and iron is admitted through tuyères usually 1 to 1½ in. in diameter, placed about 8 to 12 in. above the bottom. The tuyères are connected to a wind box having openings opposite each tuyère to permit of punching when necessary. These openings are provided with ball valves to prevent leakage of air while the converter is operating. The air is supplied at a pressure of 10 to 20 lb., depending upon the type of converter used and the depth of matte carried. The amount of air required will depend, of course, upon the grade of matte being

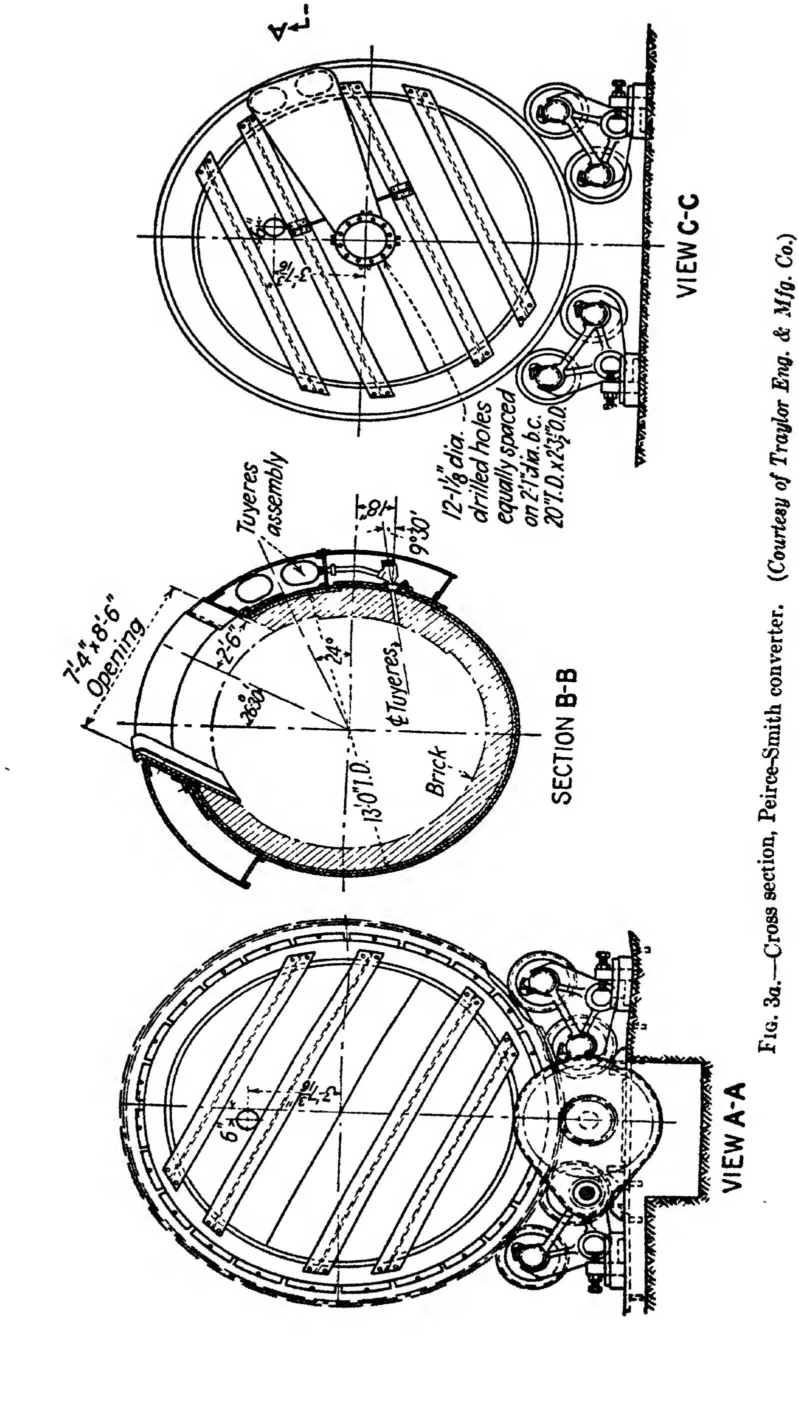


FIG. 3a.—Cross section, Peirce-Smith converter. (Courtesy of Traylor Eng. & Mfg. Co.)

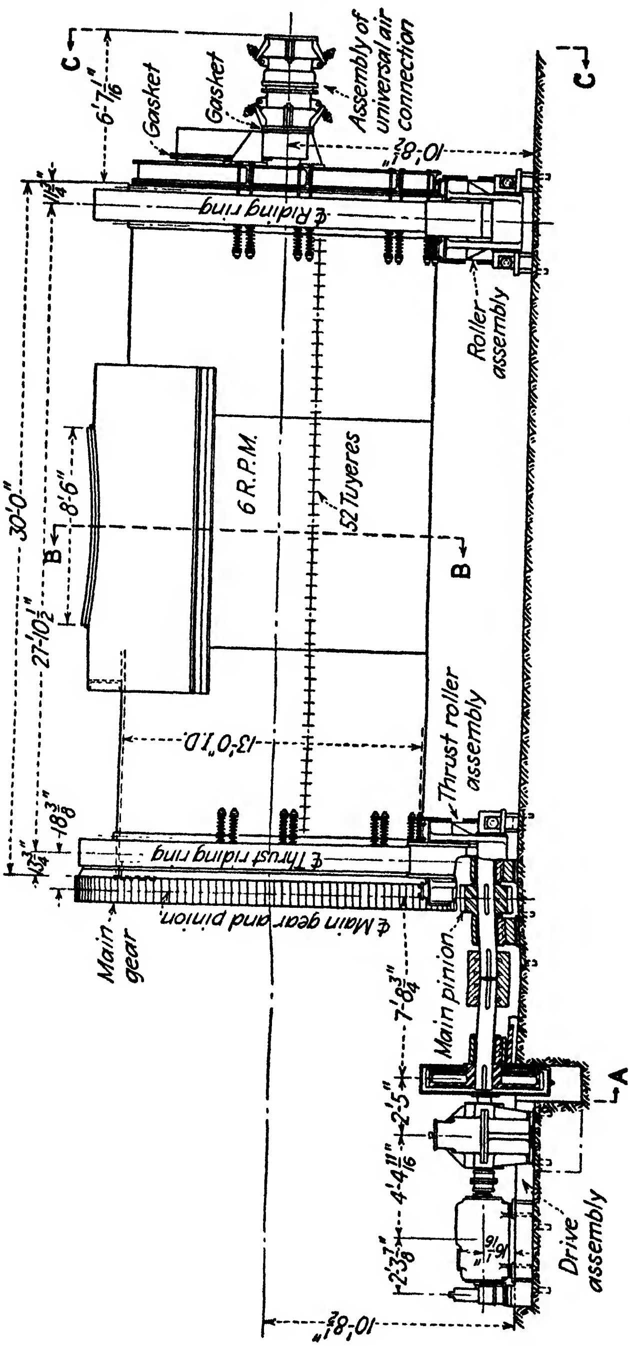


FIG. 3b.—Side view, Peirce-Smith converter, Morenci, Ariz.

converted, but will average 160,000 to 200,000 cu. ft. of free air per ton of blister produced for a 40-per cent matte.

The grade of matte that is most economical to treat in the converter depends upon the cost of the preceding operations. A low-grade matte, low in copper but high in iron, has the advantage of enabling a high temperature to be obtained owing to the fuel value of the FeS. On the other hand, the amount of iron that must be slagged requires a corresponding amount of silica, and produces a large amount of slag carrying considerable copper which is too valuable to waste and must, therefore, be re-treated for the recovery of the copper contents. The amount of copper per ton when using low-grade matte is relatively small, and the cost of treatment therefore high.

A high-grade matte, high in copper but low in iron, has the disadvantage of containing less heat, and there may be difficulty in maintaining the desired temperature.

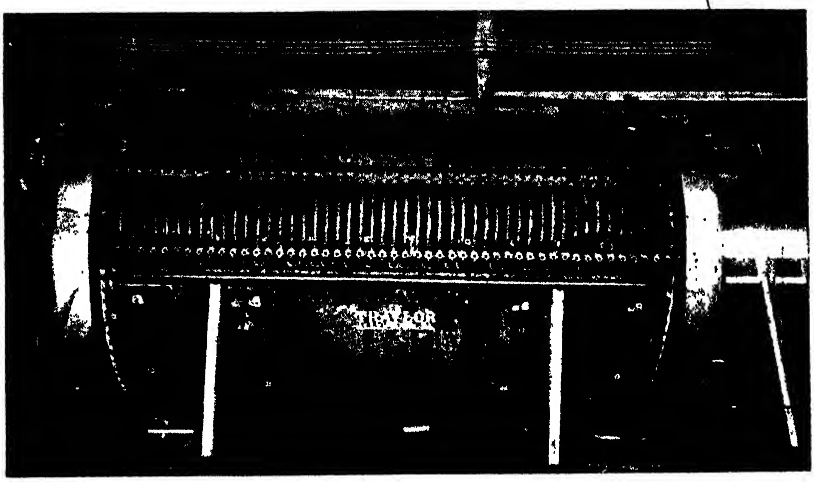


FIG. 4.—Peirce-Smith converter

The amount of slag produced is decreased with a consequent lower re-treatment cost per ton of copper produced, and the cost of converting is reduced due to the larger amount of copper per ton of matte. The economical grade is reached, other things being equal, when the cost of fluxing the iron in the regular smelting operations is less than doing so in the converter.

The operation of acid converting is conducted by first heating the converter to the required temperature by the use of wood and coke. The proper amount of matte is then introduced through the mouth, the blast turned on, and the converter turned up so that the mouth is under the hood conveying the gases to the stack. The tuyères are now below the surface of the matte and the oxidation commences. There are two main stages in the operation: (1) the elimination of the iron, or blowing to white metal; and (2) the elimination of the remaining sulphur, or blowing to blister.

During the first stage the iron sulphide is oxidized to FeO, the sulphur oxidizing to SO_2 and passing off in the waste gases. The FeO immediately attacks the siliceous lining to form the slag. Any copper that may be oxidized is immediately resulphurized by reacting with the iron sulphide. As the oxidation proceeds and the iron is slagged, the matte remaining in the converter gradually approaches white metal (Cu_2S). This change may be followed by noting the character of the flame issuing from the mouth of the converter. At the start of the operation it has a reddish color

changing to a green, and as the white-metal stage approaches, to a pale blue. If, however, an impure matte is being converted, the flame indications are unreliable, and dependence is placed on the appearance of the layer of matte on the punch rod which is inserted in the tuyères to keep them open for the passage of the blast. When the white-metal stage has been reached, it is indicated by the working of the matte on the rod.

When the iron has been slagged, the converter is turned down, the blast shut off, and the slag skimmed into a ladle. In order to determine when the slag has been skimmed clean, a rabble is held under the stream and any white metal coming over will be seen by its working on the iron of the rabble. When the slag has been skimmed, a fresh charge of matte may be introduced and the operation repeated. This is known as doubling, and is done for several reasons. If the temperature of the charge is too low, there may be danger of freezing during the finishing blow; the fresh addition of matte, therefore, gives fresh fuel with which to raise the temperature. If the matte is low grade, there may not be sufficient white metal present to cover the tuyères and, therefore, more matte must be added. If the converter cavity has become enlarged, the same condition prevails, and sufficient matte is added until the amount of white metal remaining is sufficient.

During the second stage the sulphur in the white metal is oxidized, the sulphur passing off in the gases as sulphur dioxide, the oxidized copper reacting with the remaining white metal to produce metallic copper and sulphur dioxide. The copper settles below the tuyère level and collects any silver and gold that may have been in the matte. During this period the flame of the converter changes from a pale blue to reddish brown, and the metal on the punch rod becomes more and more coppery. When the charge is finished, the converter is turned down, the blast shut off, and the metallic copper poured into a ladle for casting, or it may be cast direct from the converter. The former practice is to be preferred, as the latter causes too much delay to the converter and keeps down the tonnage treated per day.

The main objection to the acid process of converting is the rapid destruction of the lining by the union of the FeO with the silica, the latter being the sole source of silica supply. The life of an acid lining is limited to a relatively few charges, depending on the grade of matte converted, a low-grade matte being more destructive than one of higher grade, due to the larger amount of iron slagged. The expense of constantly renewing the lining was heavy, and for years efforts were made to find a lining that would not be attacked by the iron. After many attempts and failures this was successfully accomplished by Peirce and Smith.

Basic-lined Converters.—The operation of converting in the basic-lined converter is similar to the acid operation as far as the reactions go, but the silica for slagging must be supplied from some external source. As the charge of matte is in the converter, the necessary amount of siliceous ore is added, the blast turned on, and the converter turned up. The flux is generally thoroughly dried before being added to the matte to avoid explosions, though in some plants the siliceous flux is blown into the converter and spreads out over the matte in thin layers and, consequently, does not have to be dried.

The basic-lined converter cannot be operated at the temperature of the acid converter on account of the destruction of the magnesite lining at high temperatures. The lower temperature required necessitates a great deal of punching of the tuyères. With a low-grade matte there is a greater heat liberation than when a high-grade matte is being converted, and great care is necessary that the bath be not overheated. Too high a temperature retards the converting, attacks the lining, and tends to warp the converter shell. On the other hand, too low a temperature makes the tuyère punching very difficult, makes a sticky slag, and is liable to cause the formation of

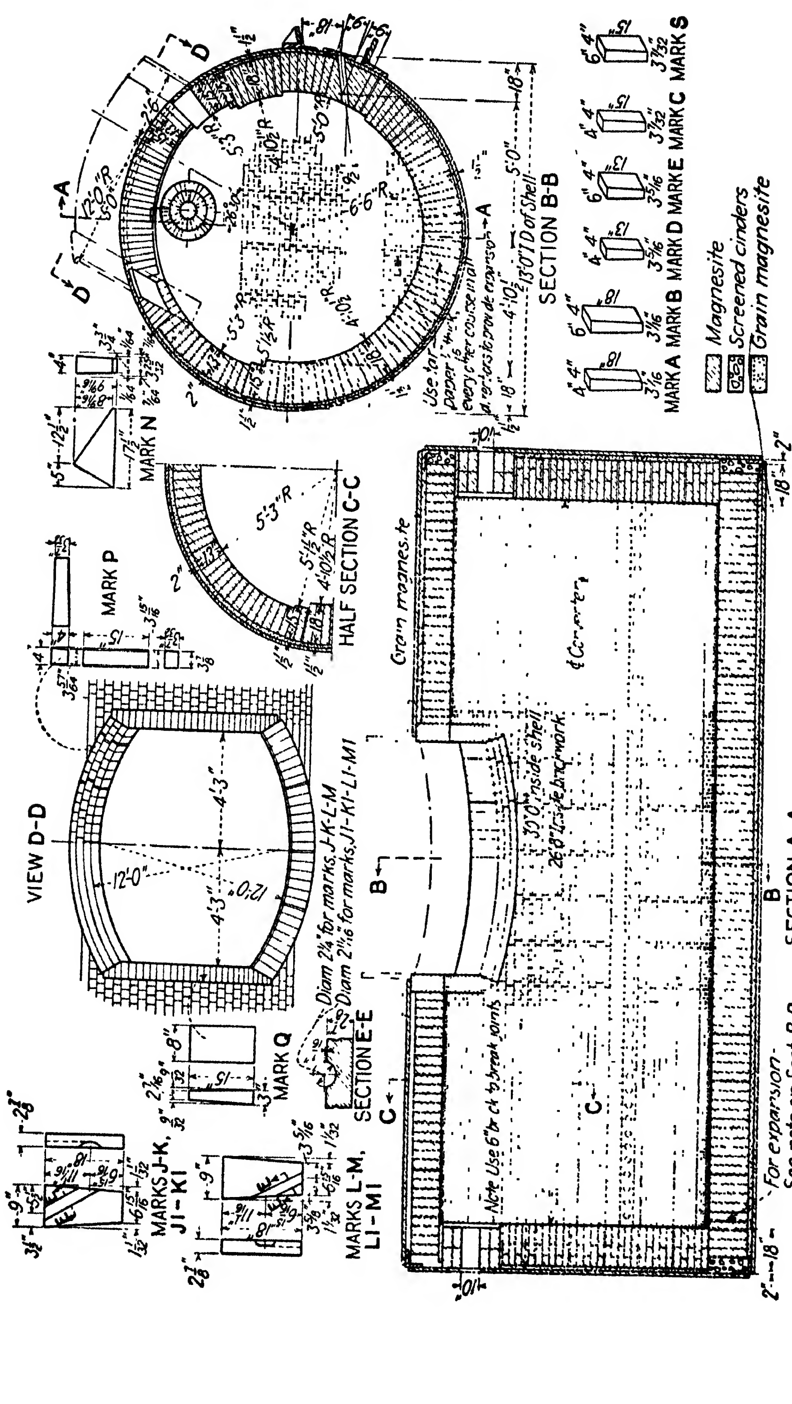


FIG. 5.—Lining of Peirce-Smith converter, Morenci, Ariz.

magnetic oxide of iron which builds up on the bottom and sides of the converter. Owing to the nature of the process, the basic converter operates at a lower temperature than the acid process, mainly on account of the large quantities of cold ore added as flux.

The critical stage of the operation is at the finish of the slagging period. If there is insufficient silica present to take care of the iron, magnetite will be formed, while an excess of silica causes a sticky slag. Magnetite is also caused by an insufficiency of silica during the blow to white metal, and this has been taken advantage of to give added protection to the lining. Wheeler and Krejci at Great Falls, Mont., patented a process of blowing a low-grade matte with either no silica or else a very small amount. This causes the iron to form magnetite, which covers the magnesite lining to almost any desired thickness and thus greatly prolongs the life. When this coating wears off in the course of the succeeding operations, it may be readily renewed during the next charge.

The main advantages of the basic converter over the acid converter are the greatly decreased cost of lining; the use of much larger converters, which make for labor and power economies; a lower-grade matte can be treated than in the acid converter; the copper in the slag is lower; low-grade ores can be used for flux that could not otherwise be treated profitably; there is less slop from the converters; and the copper is produced in a shorter time.

The slag from the converting process, containing as it does several per cent of copper, is too rich to be thrown away and is returned to the blast furnace or reverberatory, or may be treated in a slag-cleaning furnace. At some plants, it is the custom to pour the molten slag into the blast-furnace settler. This is done on account of the blast-furnace charge being so high in iron that the added iron from the converter slag is undesirable. The economy of this operation, however, is a disputed question as many metallurgists claim that the copper is not recovered to any great extent, but simply mixes with the great mass of blast-furnace slag and is lost.

Plant executives appear to rate the modern 13 × 30-ft. Peirce-Smith converter at 100 tons of copper per day for a 37 per cent matte, with an increase or decrease of 5 tons for each 1 per cent up or down in the matte tenor (within reasonable limits).

The Smelting of Oxide Ores.—Where oxide ores occur, such as in the Katanga district, these are smelted in blast furnaces with a large percentage of coke. The product is known as "black copper," and its composition depends on the impurities in the ore. A clean ore will give a high-grade copper, while, if much iron or nickel is present, these will be reduced and will lower the grade of the copper. Usually a small amount of matte is produced, owing to the sulphur in the coke or small amounts of sulphides in the ore. Where there is little or no sulphur present, the copper losses in the slag are apt to be high, while a small matte fall tends to clean the slags.

The blister copper produced from any smelting process is generally cast into slabs approximating 18 × 28 in. and 3 to 4 in. in thickness, weighing 300 to 350 lb. There is just sufficient draft to the slab to permit of its ready removal from the mold. At some plants, the practice still continues of casting the old type of Chile bar, which is about 8 × 20 in. with a thickness of 6 to 8 in. This type of bar is very difficult to sample properly, on account of the segregation of the silver and gold, and it is also a difficult pig to handle easily. The Japanese frequently cast small slabs weighing in the neighborhood of 50 lb. each, which are very expensive to handle and sample, when considered on the ton basis.

Of late years, the question of moisture in blister copper has been given considerable attention. When a slab is cast, there are numerous cavities in the interior, due to the gases. These cavities are connected with the surface of the slab by capillary tubes, and if a slab is cooled by dumping it into a bosh, considerable water may be

drawn into the cavities. It is not unusual to find slabs containing as much as 0.2 per cent moisture, and this question is the cause of much controversy between the smelter and the refiner as to what allowance should be made to cover this moisture (see page 83, Vol. I, "Principles and Processes").

In all smelting processes, more or less flue dust is produced. The roasting furnaces are the chief offenders in this respect, though they are closely followed by the blast furnaces. The reverberatories, having a relatively quiet atmosphere, do not produce much dust, while that produced by the converters is largely in the form of fume from the volatile metalloids. The collection and re-treatment of flue dust is a considerable item in the cost of operation, and every possible means is utilized to keep its formation down to the lowest point consistent with economical operation. The recovery of flue dust may be accomplished by one or more of the following methods: passing the gases through large dust chambers, in which the velocity of the gases is so reduced that all but the finest particles of dust are settled out. The gases may be filtered through woolen bags after being previously cooled to the proper temperature; this is an expensive method and requires a heavy investment in flues and baghouse. The gases may be passed through a Cottrell electrostatic precipitator in which the solid particles are thrown out of the gas stream by the action of a high-tension electrostatic field. In the Roesing system, the gases flow through dust chambers in which are suspended wires or baffles, and the dust particles impinging upon these adhere, and when sufficient has accumulated the gases are diverted into another chamber and the wires or plates are then shaken to dislodge the dust particles.

The treatment of recovered flue dust consists in briquetting and smelting in the blast furnace, a method formerly widely used but now falling into disuse; agglomerating in rotary kilns, or Dwight-Lloyd sintering machines, and smelting in the blast furnace; or in direct smelting in the reverberatory furnace—the most economical method.

Metal loss is a very important item in the smelting cost, and one that is watched and studied very carefully so that it may be reduced to a minimum. The three chief sources are dust losses in handling, metal contents of slags, and dust and fume losses through the stacks. These losses are a matter of more importance to the custom smelter than to the company owning its own mines, as in the latter case the loss is merely that of the cost of the metal to the point of loss and the potential profit, whereas in the custom smelter the miner has been paid for the contents of his ore and losses represent the loss of actual profits.

The Refining of Blister Copper.—The blister copper produced in the smelting process contains so much impurity that it is unfit for commercial consumption without refining. The following table shows the composition of various grades of blister copper produced at various smelters:

Cu %	Ag oz. p.t.	Au oz. p.t.	As %	Sb %	Pb %	Ni %	Zn %	Fe %	S %
98.8	4.50	0.01	0.004	0.002	0.018	0.41	0.016	0.15	0.10
99.5	2 50	0.02	0.035	0.015	0.001	0.04	0.002	0.03	0.06
98.8	30.25	0.31	0.10	0.040	0.150	0.050	0.120	0.25	0.17
98.4	111.9	0.295	0.02	0.178	0.001	0.005	0.003	0.13	0.20
99.10	73.3	2.09	0.01	0.01	0.048	0.005	0.036	0.056	0.25

In earlier days the refining of blister copper was performed entirely in reverberatory furnaces, but this has been entirely supplanted by the electrolytic process. Of

the former process, it is sufficient to state that it was based on the fact that when copper sulphide and copper oxide were melted together the resulting reaction formed metallic copper, the sulphur passing off in the waste gases as sulphur dioxide. Silver and gold were recovered to a considerable extent by first having a small copper fall in the matte which served as a collector for these metals together with much of the impurities present. The enriched portion was worked up separately, while the purified white metal was carried along to pure metallic copper.

The modern process of refining may be considered to be divided into the following steps: (1) A preliminary fire refining, to remove as much as possible of the impurities, followed by the casting of the copper into anodes. (2) The electrolytic process, consisting in dissolving the anode by means of the electric current and depositing the pure copper on the cathode. In this step the remaining impurities are removed, and any silver and gold contained in the anode are collected as a mud or slime to be recovered by a subsequent treatment. (3) A final furnace treatment of the cathodes, which are not in a form suitable for general commercial use, in order that they may be converted into the proper physical shape for the consumer.

Furnace Refining.—As the methods of operation of the anode and cathode furnaces are almost identical, one description will suffice for both. The furnace treatment is based upon the relatively weak affinity between copper and oxygen, as compared with the affinity between oxygen and the impurities in the copper. The process, therefore, consists in an oxidizing fusion in order to volatilize some of the impurities and to oxidize the remainder, using copper in the form of oxide as a scorifying agent. This being done, the impurities will either pass off in the furnace gases or else float on the surface of the bath as a slag which may be skimmed off.

As the remaining copper is now saturated with oxygen, the next step is to reduce the cuprous oxide to copper by means of some satisfactory reducing medium, after which the copper is cast into the necessary shapes.

In the anode furnace the blister copper should be refined to the highest degree that is economically possible in order to have a uniform high-grade product to send to the electrolytic process. This is necessary, as the success of the latter is largely governed by having uniform operating conditions, and it is generally much cheaper to eliminate impurities by a furnace treatment than by electrolytic methods. It is, however, not possible to remove the last traces of the impurities in the furnace. The great bulk is gotten rid of quite easily, but as the amount becomes reduced it becomes increasingly more difficult without slagging off so much of the copper that the treatment of the resulting by-products becomes too expensive. Just where this point is depends upon local conditions and the relative cost of the two processes. There are also some of the impurities that tend to alloy with the copper and are removed with great difficulty.

The reverberatory furnaces in which the refining is conducted are at the present time constructed with capacities of 500,000 to 600,000 lb. per charge. Owing to the weight of metal contained, they are necessarily of much stronger construction than the reverberatory furnaces used in the smelting of ore. The side walls are constructed of silica brick with a thickness of 12 to 18 in., though there is an increasing tendency to use magnesite brick up to a point above the metal line, and then use silica or a good grade of clay brick from that point up to the roof.

The roof is almost invariably made of silica brick 15 to 18 in. in thickness, though attempts have been made to use firebrick or chrome brick. The great advantage of silica brick is its ability to withstand the temperatures obtained without softening and losing its shape. Firebrick softens at a low temperature, particularly when under pressure, while chrome brick absorbs a great deal of metal, and it is difficult to treat the burned-out brick for the recovery of the copper contents.

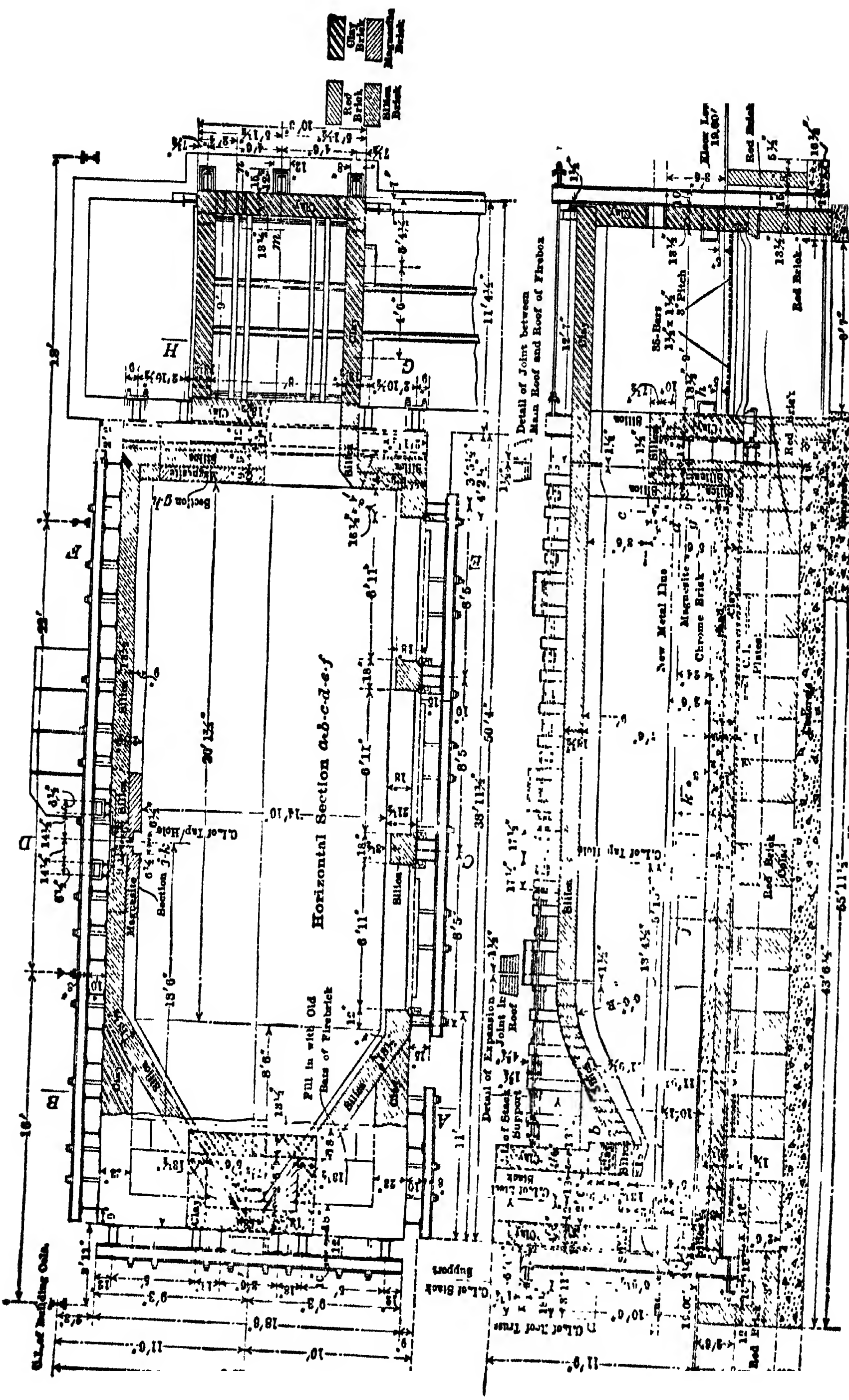


FIG. 6.—Copper refining furnace, United States Metals Refining Co., Carteret, N. J.

The hearths of furnaces treating relatively pure materials are generally constructed of siliceous material, while magnesite brick is used where the copper contains considerable amounts of lead or antimony. The siliceous hearth is generally made of high-grade silica sand which has been crushed to the size of coarse sand. It may be used with an admixture of lime or copper oxide or may be put into place without any binder other than the natural impurities in the sand itself. The sand is mixed thoroughly and placed in the furnace, where it is given a thorough calcining, after which it is spread over the bottom to the desired depth and tamped down. The furnace is then gradually brought to the highest possible heat that the brickwork will stand until the new bottom is thoroughly sintered into place. Then the furnace is gradually cooled down, and the bottom is then seasoned by covering it with a thin layer of scrap copper, melting this, and allowing it to soak into the bottom. The furnace is allowed to cool somewhat and the operation repeated until the copper that will be quickly absorbed has been taken up. After this, small charges are introduced and the furnace is gradually brought up to capacity in the next few days. It is found that a furnace will absorb copper for a considerable period of time before becoming saturated. The amount of copper locked up in a bottom will depend on the size and the shape of a furnace, but may be said to be in the neighborhood of 1000 lb. per ton of daily capacity. The concentration of silver and gold in a furnace bottom will depend on the grade of material treated, but will increase with continued use, the gold tending to concentrate to a greater extent than the silver. Very high silver charges will greatly increase the silver absorption, which will not be washed out by later charges of lower grade to any considerable extent.

Owing to the danger of overheating the bottom and having a portion of it come up, the universal practice is to have a vault under the bottom to ensure the proper amount of cooling. This may be supplemented by having pipes laid in the bottom through which air or water is forced to ensure the necessary cooling. A bottom of magnesite brick will radiate more heat than a silica bottom, owing to the greater heat conductivity, and in such construction it is necessary to have the magnesite brick underlaid with a heavy backing of clay brick. This type of bottom is generally laid in the form of an inverted arch held in place by skewbacks attached to the side plates of the furnace. The brick should be laid dry or in a mixture of powdered magnesite and linseed oil. After laying it, the furnace must be very carefully dried out by the use of salamanders placed at different points along the hearth until all moisture has been driven off. If this is not done, there is great danger of the formation of superheated steam, which destroys the texture of the brick, and the entire bottom is liable to be rapidly destroyed. After drying out, the furnace is gradually brought up to a good red heat and the bottom seasoned as with a silica bottom.

The fuel used may be bituminous coal, pulverized coal, fuel oil, or gas. The modern tendency is to use either fuel oil or powdered coal. Hand firing is expensive, and ash disposal is bothersome. Powdered coal has the disadvantages of requiring the installation of a pulverizing plant, and as much of the ash of the coal remains in the furnace, the amount of slag produced is increased. Fuel oil has the disadvantage of requiring the installation of storage tanks, pumps, and preheaters for the oil. Either powdered coal or fuel oil is more economical than hand firing with an equivalent B.t.u. price, and the furnace temperature is much easier to control.

When hand firing with bituminous coal, the coal used will approximate 250 to 350 lb. per ton of copper; pulverized coal will reduce this 20 per cent, and with fuel oil the consumption will be about 22 to 26 gal. per ton, using oil of 18,000 B.t.u. per lb. and 16 to 18°Bé.

It is now the universal practice to equip all reverberatories with waste-heat boilers to recover the large amount of heat in the waste gases. With coal, the recovery will

be 6 to 8 lb. of steam per pound of coal and with oil, 8 to 10 lb. of steam per pound of oil. In a large plant this waste-heat steam amounts to one-third to one-half of the steam used in the plant, so that the economy is obvious.

The dimensions of some refining furnaces are:

General Dimensions of Some Refining Furnaces[1]

	American Smelting & Refining Co.		Raritan Copper Works		U. S. Metals Refining Co.
Length of hearth	50 ft.	36 ft.	37 ft. 6 in.	43 ft.	40 ft. 3 in.
Width of hearth	14 ft. 7 in.	15 ft.	17 ft.	14 ft. 3 in.	14 ft. 4 in.
Depth of hearth	22 in.	14–16 in.	35 in.	28 in.	30 in.
Hearth area, square feet	665	490	559	553	496
Length of grate	9 ft.	Oil fired	Oil fired	....	8 ft. 3 in.
Width of grate	8 ft. 4 in.	....	....	....	7 ft. 4½ in.
Area of grate, square feet	75	....	....	....	60.8
Height of roof above hearth at bridge	6 ft. 4 in.	6 ft. 10 in.	7 ft. 9 in.	7 ft. 6 in.	7 ft. 2 in.
Height of roof above hearth at flue	3 ft. 6 in.	3 ft. 6 in.	5 ft. 10 in.	4 ft. 2¾ in.	4 ft. 9 in.
Area of flue, square feet	12.47	12.00	11.50	9.15	12.75
Tons output per 24 hours	200	178	250–275	275–325	226

[1] "Metallurgy of Copper," Hofman-Hayward.

The various operations of the furnace may be classified as charging, melting, oxidizing, poling, and casting, and will be taken up in their order. The large furnaces are charged by means of electrically operated charging machines which handle up to 6000 lb. of copper at one time and which will charge a 200-ton furnace in less than 2 hr. In the smaller installations the old method of hand charging is still in use. This consists of placing the slabs of copper on a paddle and sliding them into the furnace. This is a slow and expensive method and is rapidly being displaced. Owing to the large amount of space occupied by the slabs, the amount that can be charged at one time is usually less than the capacity of the furnace, and it becomes necessary to recharge a small amount after the original charge has been melted down.

At the plant of the Ontario Refining Co., molten blister copper is conveyed 1¼ miles from the smeltery to the refinery in a specially designed car holding 70 tons of hot metal. This car is spotted alongside the furnace and the contents poured therein through a launder.

When charging cathodes, a larger amount can be charged during the first charging, as they stack better and do not occupy as much space relatively. At the plant of the Nichols Copper Co. a unique method of charging is used, which consists of sliding the cathodes into the furnace by means of a chute. By this arrangement, the furnace is not permitted to cool down, and the fuel consumption is thereby decreased. With the charging crane the doors of the furnace must be opened, and by the time the furnace is charged it has cooled down to a dull red or black heat.

When the charging of the furnace has been completed, the doors are luted up and the fire urged to the utmost extent. As copper is an excellent conductor of heat, the metal rapidly absorbs the heat and soon starts to melt on the edges. During the melting, the flame is kept strongly oxidizing in order to have a sharp cutting heat

and to form as much oxide as possible. When the surface of the bath is smooth, the firing is continued strongly until the metal on the bottom has melted, which is recognized by the charcoal or coke covering of the preceding charge rising to the surface. Between the time when the charge is flat and when the metal is afloat, the slags that form are skimmed. The amount of slag formed depends on the nature of the material charged. Average blister copper will produce about 3 to 4 per cent of its weight of slag, cathodes about 1 to 2 per cent, and foul coppers may run as high as 30 per cent. With coal firing the ash of the coal is frequently blown over into the bath and forms slag, and with powdered coal there is a considerable increase, at times amounting to 50 per cent. Fuel oil, on the other hand, has no tendency to increase the amount of

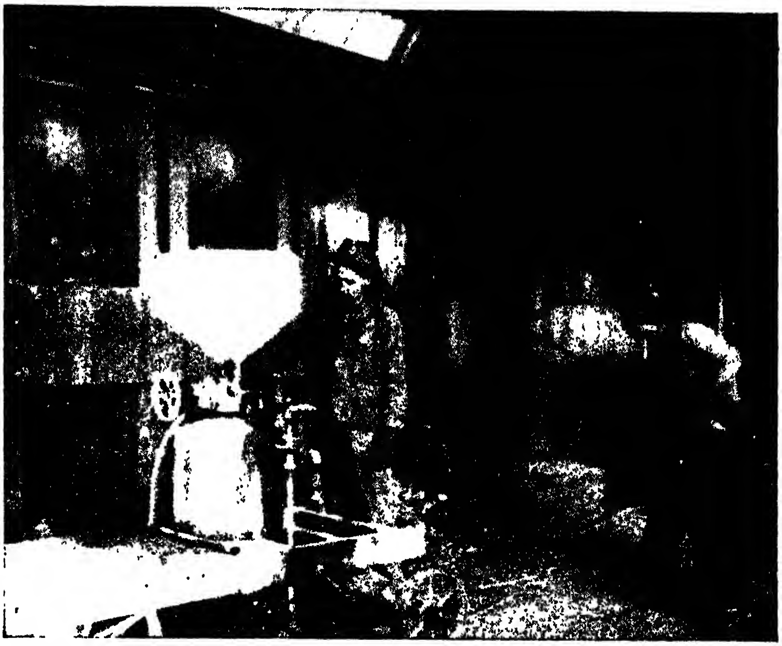


FIG. 7.—Application of silica slurry, Clarkdale smeltery, Phelps Dodge Corp.[1]

slag formed. As refinery slags are high in copper (30 to 50 per cent), it is seen that the re-treatment charges are heavy, and a small increase in the amount of slag formed is immediately reflected in higher costs.

When the metal in the bath has been skimmed clean, a say ladle, which is a small ladle with a long handle used for taking samples of the molten metal, is dipped into the furnace, and a test button taken to determine the condition of the metal If, while the button is solidifying, it breaks through the crust and "throws a worm," this is indicative of sulphur, and a green pole is inserted in the bath to agitate the metal and drive out the sulphur held in solution by the copper. During this poling the atmosphere is kept strongly oxidizing. Buttons are taken frequently until the evidences of sulphur have disappeared. This operation is known as poling down. When the sulphur has been poled out, the copper in the bath is oxidized by inserting air pipes through which compressed air is forced. This not only itself oxidizes the copper to a considerable extent, but, by the violent agitation it causes, exposes a

[1] Figs. 7 and 8 are from R. A. Wagstaff's "Changes and Improvements in Modern Copper Smelting," T.P. 1609, *Trans. A.I.M.E.*, Feb., 1944.

large surface of the molten metal to the oxidizing influence of the hot gases. To assist the oxidizing, a rabble may be introduced through the skimming door and by means of a chain suspension swung back and forth the surface of the metal broken into thin sheets or sprays. It is found that the rabble is more effective as a means of oxidizing than the air jets, but, owing to the great mass of copper to be oxidized and the hot and fatiguing work of swinging the rabble, its use as the sole means of oxidizing is impracticable.

During this period of blowing and flapping, buttons are taken to show the progress of the oxidation. As the amount of cuprous oxide in the bath increases, the surface of the button sinks and the fracture shows a color approaching a brick red. When the metal is saturated with oxide, there will be a deep depression, the fracture will show a bubble in the center, and the fracture will be coarsely cubical and a strong brick-red color. During this period, more or less slag will form and will be skimmed off, so that the surface of the metal will be kept clean for the action of the hot oxygen in the gases. The cuprous oxide formed acts as a scorifying agent and is the effective means of removing the impurities in the metal.

When the buttons show that the charge is saturated with oxygen or "set," the air pipes and rabbles are removed and the surface of the bath is covered with coke or charcoal. The doors are closed and tightly luted up so as to prevent the admission of excess air. A pole is then inserted in the bath in order to reduce the cuprous oxide to metallic copper.

The poles used for this operation are usually hardwood, but softwood is readily usable, the chief objection being the heat developed at the poling door, with the attendant discomfort to the men, and more wood is required per ton of copper. An average amount of wood used for poling may be considered to be 100 to 150 lb. per ton of copper. If wood is used to make the charcoal covering for the bath, the amount is increased to 250 lb. per ton. As the pole burns away, it is pushed further into the furnace, and when it becomes too short to hold by the chain block, it is pushed into the furnace and becomes a brand, while a new pole is introduced.

During this time, test buttons are taken and the surface and fracture observed. The fracture gradually changes from coarsely cubical to finely granular, then fibrous, the color changing from a brick red to a salmon pink. When the poling is finished, the surface of the button is slightly rounded, and the fracture is silky and of a rose color. The copper is now said to be "tough pitch" and is ready for casting.

During the progress of the refining the various impurities behave about as follows: Iron and cobalt oxidize and slag off readily, though if cobalt is present in any considerable quantity a considerable time may be required for its complete elimination.

Nickel is a very difficult element to slag on account of its strong affinity for copper. With high-nickel coppers the first few percentages of nickel readily pass into the slag, but as the amount decreases the slagging becomes slower and slower. To eliminate the last portions is extremely difficult. The bath must be skimmed clean, and, by continuing the oxidation, the nickel oxide forms as a powder and may be skimmed off. If, however, there is any reducing action in the furnace, the nickel easily reduces and is absorbed by the copper.

Sulphur requires a great deal of poling and oxidizing to effect its removal, and if present in blister copper to any considerable extent will make the furnace work very hot. If an excessive amount is present, there will result a great deal of trouble from the formation of matte on the surface of the bath.

Lead partly volatilizes and is partly slagged. With considerable lead present it may become necessary to throw the charge coarse with a small addition of matte and reoxidize. When present in any considerable quantity, lead will vigorously attack silica bottoms as soon as any oxide is present, and it may become necessary to use

magnesite brick bottoms when handling blister high in this element. Zinc is readily oxidized, and its elimination is simply a question of time of blowing.

Arsenic and antimony partly volatilize, but are eliminated with considerable difficulty. In some cases it becomes necessary to treat the bath with a flux of lime and soda in order appreciably to reduce the amounts of these undesirable elements. In severe cases it is necessary to give the copper a second refining.[1]

When the metal is finally ready for casting, that from the fire refining of blister copper is cast into anodes for the electrolytic process. For the multiple system these are slabs 24 × 36 in. or 36 × 36 in. and about 2 to 3 in. in thickness. When used

FIG. 8.—Suspended arch in reverberatory furnace, Hudson Bay Mining & Smelting Co.

for the series system, the anode may be cast as a slab for rolling, or as a long thin anode for direct dissolving.

When the anode is to be used direct, lugs are cast so that it may be easily supported from the conductor bar or hanger bar. In some cases, loops of heavy copper wire are placed in the mold and the metal cast around them. A heavy copper bar is passed through the loops and is used to make the contact.

When small furnaces are in use, the copper is frequently cast by hand ladling, but with the increased size of the furnaces it becomes necessary to find some faster method. It is now the universal practice with large furnaces to draw off the metal from the side or end of the furnace through a tapping slot. This slot or taphole is filled with a mixture of clay sand and a small amount of coal, hard enough to withstand the pressure of the metal on the interior of the furnace, but soft enough to permit of cutting a gutter for the flow of the metal. This plug is held in place during the working of the furnace by transverse iron bars, about 1 in. square, placed on top of one another

[1] For researches on relative slaggability, see *Mineral Ind.*, p. 248, 1901.

and held by guides fastened to the side plates of the furnace. These bars are removed at the time of casting, and the clay plug is cut away from the top sufficiently to permit the copper to flow over the edge into a launder leading to the ladle. As the level of the copper in the furnace falls, the clay plug is cut down more and more. If at any time it is desired to stop the flow of metal, a ball of clay is placed in the taphole and pressed down with a stick.

In the new Phelps Dodge plant at Morenci, the anode furnaces are of the tilting type, 13 × 25 ft., holding about 175 tons. They are set at a height sufficient to permit complete emptying into the pouring spoon. Complete rotation is possible, and gears, riding rings, cradles, and drive are interchangeable with similar parts of the converters. The lining is 18 in. of magnesite brick in the lower half and 13 in. magnesite in the upper half, backed up by insulating brick to reduce heat loss. The low-pressure gas burner is mounted on a hinge to permit swinging away from the port. Only a short movable flue is provided, without a stack, to avoid undesirable draft.

There are several types of casting machines for the casting of anodes. The Walker wheel has the molds on the circumference of a wheel approximately 21 ft. in diameter. The wheel is turned by hydraulic or electric power, and the molds are brought under the furnace ladle where they are stopped while the mold is filling. The wheel is then revolved until the next mold is under the ladle. When the newly cast anode is about three molds away from the ladle, it is sprayed with water to cool the metal, and at the same time the mold is cooled by a spray from underneath. When the anode is nearly opposite the ladle, it is lifted from the mold by means of a push pin which passes through the mold and slides on an inclined track. The anode is then lifted from the mold by a crane and placed in a bosh filled with running water in order to cool to the room temperature.

The straight-line casting machine consists of a series of molds carried by an endless belt in front of the ladle. When a mold is filled, it passes toward a bosh, being sprayed on its journey, and at the end of the belt where the molds pass underneath, the anode is either dumped into the bosh or else lifted out of the mold by a crane and placed in the bosh for cooling.

In hand ladling, the ladle man stands in the center of a wheel somewhat similar in shape to the Walker wheel, and, as each mold passes, it is filled with copper and passes around to the rear, where it is cooled and removed either by a hoist or by a man using a long-handled lifter.

Anode molds are generally made of copper, though in some instances cast-iron molds are used. The advantage of copper lies in the fact that when the mold has outlived its usefulness it can be charged into the furnace and the copper recovered and sold at market value, while a cast-iron mold has only a low scrap value. In order to prevent the copper from sticking to the molds, they are washed with pulverized silica, which is applied at such a point that the heat of the mold will dry it out before the ladle is again reached.

The furnace refining of blister copper should be carried to the highest possible point in order to produce the best results in the electrolytic refining. A well-refined anode will dissolve readily and evenly and will give a good deposit, while an improperly refined anode will dissolve unevenly and give rough deposits and a heavy percentage of scrap which has to be re-treated. It has been very clearly demonstrated that any extra expense incurred in the anode refining to ensure a high-grade product will result in a much greater saving in the balance of the refining process.

The electrolytic refining of copper is based on the selective action of the electric current in the following manner. If two metal plates are suspended in an electrolyte, and a direct current is passed from one plate to the other, the metal of the plate where the current enters, known as the anode, will be dissolved, provided the composition

of the electrolyte is of the proper type. The plate at which the current leaves is known as the cathode, and what happens at this point depends on the nature of the dissolved metal and the composition of the electrolyte. The constituents of the

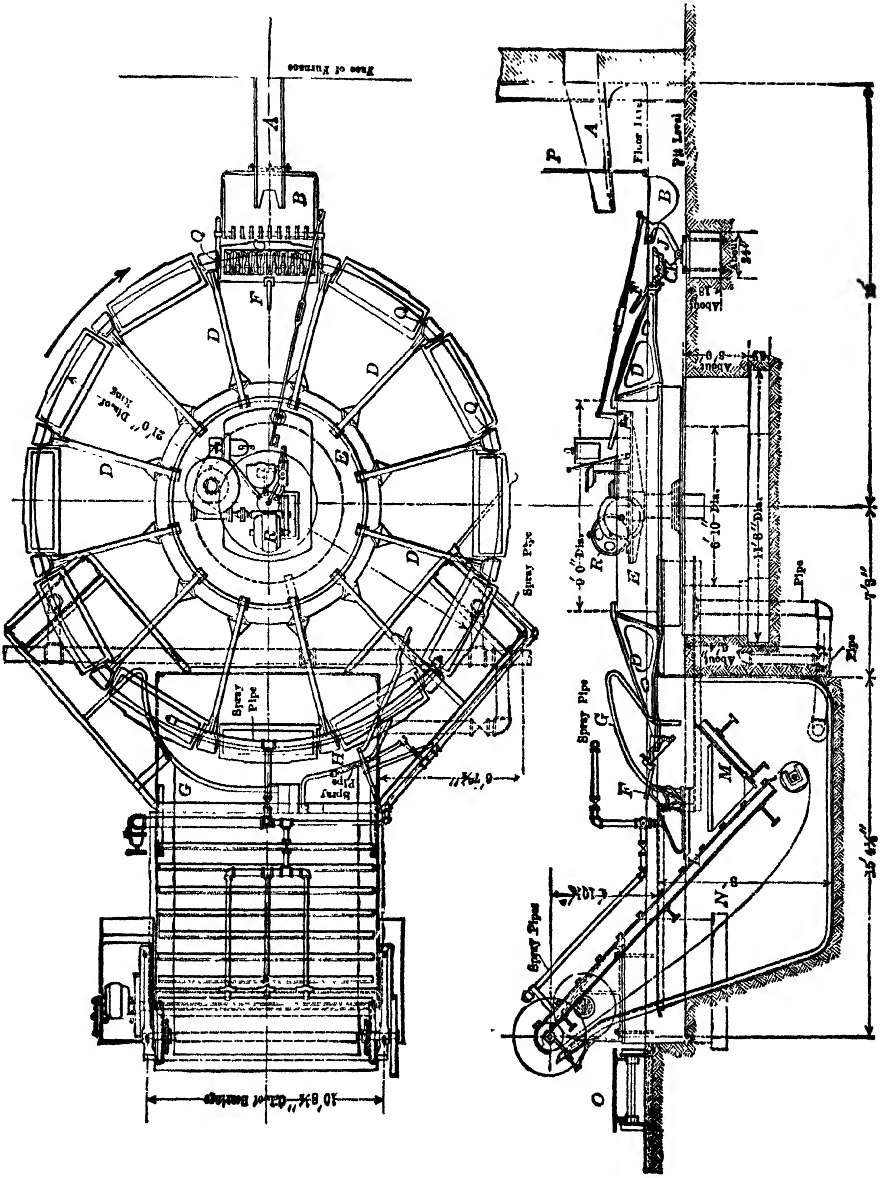


FIG. 9.—Walker casting machine

electrolyte are partly ionized, and the individual ions have definite discharge potentials depending upon their positions in the e.m.f. series (see page 378). Those ions having the lowest discharge potential will be discharged as long as they exist in sufficient amounts to carry the current. If there is an insufficient amount, the ion next highest will be discharged. In an aqueous electrolyte the hydrogen ion is presen

and will be discharged unless there is present some other ion standing below it in the series. Copper is in this position and, therefore, will be discharged before hydrogen. The electrolytic refining of copper is, therefore, based upon the fact that, if a copper anode is suspended in an electrolyte composed of copper sulphate and sulphuric acid, it will be dissolved and the copper pass into solution. At the cathode, which is also copper, the copper in solution will be deposited while the hydrogen present will be unaffected.

The impurities associated with the copper in the anode do not deposit on the cathode because they stand higher in the e.m.f. series than either copper or hydrogen and, therefore, while they dissolve in the electrolyte, remain in solution, or else the composition of the electrolyte is so adjusted that they remain on the anode as insoluble alloys or compounds.

The impurities that, as a rule, pass into solution and remain there are Fe, Ni, Co, Zn, As, and Sb. Those that are insoluble and remain on the anode as a slime are Ag, Au, Pt, the rare metals, and Se, Te, and Pb.

Where an impurity exists in the anode as a chemical compound it will tend to pass into the slime, as chemical compounds have a much lower electrical conductivity than the copper, and these compounds largely segregate in the anode. The purer metal immediately surrounding them is dissolved, allowing the compound to fall into the slime, where it may lie inert or else be slowly attacked by the electrolyte and pass into solution. Those elements which alloy with copper may either dissolve or pass into the slime, depending upon their nature and properties.

Two systems of electrolytic copper refining are in use at the present time, the multiple and the series, differing in the arrangement of the electrodes.

The Multiple System.—In the multiple system, the anodes and the cathodes are connected in multiple and are suspended crosswise in a lead-lined tank. The anodes are generally 2 × 3 ft. or 3 × 3 ft. in area and 2 to 2½ in thick, weighing 400 to 600 lb. The number of anodes varies from 26 to 32 per tank, and they are given a spacing of about 4 in.

The multiple cathodes consist of pure copper starting sheets suspended between the anodes. The preparation of the starting sheets is an expensive operation, requiring skilled labor. In the manufacture of the starting sheets, anodes of the purest grade of copper are used, and the anode is wider than the regular anodes to ensure the edges of the starting sheet being perfect. The starting sheet is made by depositing copper on a rolled and stretched copper blank, which is coated with a mixture of graphite and oil, or else gasoline and oil, or other mixture that has been found to be satisfactory for the purpose. This coating is for the purpose of allowing the sheet to be readily stripped from the blank. To prevent copper being deposited on the edges of the blank, these are protected by covering them with grooved strips of wood, which are removed when the sheet is stripped from the blank, or else the edges of the blank are painted with a heavy asphalt paint, and a shallow groove is cut in the blank at the point where it is desired to have the sheet break off.

The process of manufacture of the starting sheet consists in first giving the blank a coating of the oil paint; the edges are then painted with asphalt or the wooden strips put in place, and the blank is hung in the tank while the current is on, and allowed to remain for the necessary time, usually 24 hr. The blanks are then drawn from the tank one at a time. The operator strips the thin sheet from the blank with a sharp-edged knife, one sheet from each side, repaints it, and it is returned to the tank. The thickness of the sheet is usually about $\frac{1}{16}$ in., and a 3 × 3-ft. sheet will weigh about 10 lb. It is of the greatest importance that the current be flowing when the blank is placed in the tank, or else the oil will be washed off by the hot electrolyte and the new deposit will be burned fast to the blank when the current is turned on. In

order to hang the starting sheets in the regular depositing tanks, two loops are fastened to each sheet. These loops are made of starting sheets which are cut into the proper-size strips and are fastened to the sheet by punching and bending back the sharp corners of the punched portion.

As the starting sheets must have good tensile strength, they are usually made at a current density lower than that used in the regular tanks, and the electrolyte used is kept very pure. The number of tanks required for this work will depend upon the number of cathodes to be drawn daily from the regular tanks, as a starting sheet must be produced for each cathode drawn.

The tanks used for the multiple system are made of wood or reinforced concrete, the latter being preferred in recent installations. All tanks are lined with 6 per cent antimonial lead to protect the wood or concrete from attack by the electrolyte. The dimensions of a tank for 30 anodes with a surface of 3 × 3 ft. is approximately 11 ft. long by 3½ ft. wide by 3½ ft. deep. Several arrangements of tanks are in use at the present time, the earlier arrangement being two tanks side by side and in rows depending upon the size of the tank room. As this arrangement required a large amount of copper to be tied up in bus bars, the Walker arrangement was developed, in which there are but two rows of tanks, but there are 15 to 20 tanks, having a common partition, in each row. As the electrodes of one tank are connected to the electrodes of the adjoining tank by the use of a light triangular bar to which the cathodes of one tank and the anodes of the next tank are connected, there is a great saving in copper. This arrangement is at present the most widely used.

The tanks are built on masonry piers high enough to permit of proper inspection underneath for leaks, etc. At the top of the piers are glass blocks having a thin sheet of lead placed on the top. The glass block serves as an insulator; the lead sheet protects the glass from any drip from a leaky tank. The tanks rest on longitudinal sills 8 × 8 in., which rest upon the top of the piers. There are many variations in the constructional details of the tanks, each refinery having its own ideas on the subject.

The electrical connections depend on the tank arrangements. In the older system where two adjacent tanks are arranged in cascade of 8 to 10, the current is led to each pair of tanks by a heavy copper bus bar. The current leaving the cathode bar was conducted to the adjacent tank by means of a heavy copper connection plate upon which the anode bar rested. The current then left this tank through a heavy bus bar which led it to the next pair of tanks in the cascade. In the Walker system the current is led to the first tank by a heavy bus bar. The common partition between the tanks supported a light triangle bar upon which the cathode bars of the preceding tank and the anode bars or lugs of the succeeding tank rest. At the end of the row of tanks the current was carried by a heavy bus bar to the next row of tanks. There is thus a great saving in the amount of copper tied up in conductors when using the Walker system.

In the multiple system, as the electrodes are in multiple, each anode must have its individual current supply. With a depositing surface of 540 sq. ft. and a current density of 20 amp. per sq. ft., the total current required will be 540 × 20, or 10,800 amp. per tank. With 30 anodes per tank, each anode will require 360 amp. The use of such large currents requires conductors of large cross section to prevent overheating and consequent loss of power, and this constitutes a large proportion of the initial investment in a multiple tankroom. The generation of currents of this magnitude also requires expensive generating equipment in the powerhouse.

The operation of the multiple system is about as follows: The anodes, having been straightened, are placed in the tank by an overhead crane and are then evenly spaced by the tankmen. The starting sheets are straightened and a copper bar passed

through the loop. They are then hung in the tanks and the loops securely clamped to the cathode bar by tongs specially designed for this purpose. This is done to ensure a minimum contact resistance between the loop and the rod. The starting sheet is then accurately spaced between the anodes. All anode and cathode contacts with the bus bars or triangle bars are then given a coating of oil in order to prevent acid and salts from creeping in and spoiling the contact. The tank is then filled with electrolyte and the current turned on. At the end of 48 hr. it is customary to withdraw the cathodes one by one and straighten them, as the initial deposit has a tendency to make them curl slightly.

The time required for making a full-weight cathode depends upon the current density used, the quality of the anode, and various factors peculiar to the plant in question; but usually two cathodes are produced from each anode, and the time required per cathode is 10 to 14 days. During this time the tanks are gone over daily and inspected for short circuits, and when these are found the cathode is lifted up and the nodule causing the short circuit broken off, or else it may be removed by the tankman's sweeping a copper rod across the face of the cathode.

When the first crop of cathodes has run its full time, the tanks are cut out of circuit by short-circuiting the entire section of tanks to be drawn by the use of a heavy copper cutout. The cathodes are removed by an overhead crane and taken to a wash box, where they are thoroughly washed by a spray of hot water to remove any adhering slime and electrolyte. They are then piled on a car and sent to the wire-bar furnace.

The anode mud that contains the silver and gold is then swept from the face of the anode by means of brushes with long handles, or else the anode may be withdrawn from the tank and taken to a wash box, where the slime is washed off by hot water and the anode returned to the tank. A new set of starting sheets is placed in the tank, the contacts gone over as before, and the current turned on. During this second run of cathodes, the anodes are carefully watched to see when they become too thin for proper working. When an anode gets scrappy, due to its being thinner than it should be, or else having dissolved at a faster rate than its mates, it is withdrawn from the tank and replaced by a piece of heavy scrap, a supply of which is kept on hand in the tankroom for such purposes.

At the end of the run the tank is cut out of circuit as before, the cathodes removed, washed, and shipped, and the scrap anodes drawn from the tank by the crane and thoroughly washed to remove all adhering slime. They are then sent back to the anode furnace for remelting. Any heavy scrap is generally kept in the tankroom for the purpose, described above, of replacing anodes that have gone scrappy before their time.

The electrolyte is pumped out of the tanks, a plug in the bottom of each tank is removed, and the accumulated slime is flushed into a launder, which conveys it to a slime tank, where it is screened to remove coarse pieces of metallic copper and is then pumped to the silver refinery for the recovery of the precious metals contained.

The tank is thoroughly cleaned of all adhering salts and slimes, any leaks that may have developed are repaired by the lead burners, the triangle rods are cleaned of salts and dirt, and the tank is then ready for another run.

The amount of scrap made in the multiple system will depend on the character of the anode, the current density, and the care taken in casting the anodes uniformly thick. The usual practice will make about 15 to 20 per cent scrap, a large part of which is accounted for by the lugs that are undissolved. The percentage of scrap made is kept as low as possible on account of the re-treatment cost, the tie-up in metals, and the delay to putting in process contract material.

The Series System.—In the series system the electrodes are connected in series and the same current serves each electrode. There are no starting sheets as the back of each anode serves as the cathode for the preceding anode.

There are two modifications of the series system: In one a rolled anode is used, in the other a cast anode is used. The first is in operation at the plant of the Baltimore Copper Co., the second at the plant of the Nichols Copper Co.

At the Baltimore plant the anode material must be of good quality to permit of rolling without cracking. The anode furnaces cast a slab, which, while red hot, passes through the rolls and is rolled down to a thickness of about 14 in. It is tnen cut into plates approximately 11 × 24 in., which are straightened and two plates placed in wooden frames, which are placed in the tank. The tanks are 11 ft. 6 in. in length, 25 in. in width, and have a depth of 26 in.; 135 electrodes are placed in each tank.

The current enters the tank through the first electrodes, passes through all the electrodes in series, and leaves through the last electrode, which is a copper plate. The electrodes act as both anodes and cathodes, the side receiving the current being the cathode, and the side from which the current leaves being the anode. As a result, the impure metal of the anode is dissolved from one side of the plate while pure copper is deposited on the other side of the plate to approximately the same thickness.

The deposition is finished when the anode has been dissolved to the desired degree, which is usually a complete dissolving, so that there is little or no scrap, other than that from the rolling and the cutting of the plates and that left in the grooves of the strips. The cathodes are removed from the tank, washed, and sent to the wire-bar furnace. The slime remaining at the bottom of the tank is removed by hand and the tank is carefully cleaned out before the next run.

At the Nichols plant the anodes are cast, and average 12 × 54 × $\frac{5}{8}$ in. They are straightened, and the cathode side is painted with a mixture that will permit of readily stripping the cathode from the undissolved portion of the anode. The anodes are then hung on an iron bar, there being five anodes to a bar, and 121 bars are hung in a tank. The tank is then filled with electrolyte and the current turned on. When the deposition has proceeded to a point where the amount of anode remaining is about 8 per cent, the deposition is considered finished; the electrodes are removed from the tank by a crane and carried to the stripping room, where the remaining anode scrap is removed and sent back to the anode furnace for re-treatment, the cathodes being sent to the wire-bar furnace, and the slime flushed out and sent to the silver refinery.

The current density used in the series system is the same as that used in the multiple system, but as the electrodes are in series the amount of current per tank is much less. Where a multiple tank having a depositing surface of 540 sq. ft. requires a current of 10,800 amp., a series tank having a depositing surface per plate of 4 sq. ft., as at Baltimore, or 23 sq. ft., as at Nichols, will require 80 or 460 amp., respectively. These small currents avoid the use of conductor bars of large cross section, and, as there are but few contacts per tank in the series system as against approximately 120 in the multiple system, the contact losses are reduced to a minimum.

The voltage across the electrodes in the series system at the solution level is approximately the same as that in the multiple, for equal spacing, so that, while the multiple system has a low voltage per tank, the series system, which in reality consists, electrochemically, of a number of multiple tanks in series, has a voltage corresponding to the number of electrodes in series. Where the multiple system has a voltage at the solution level of, say, 0.2 volt, the series tank, with 135 electrodes, will have a voltage of 27.0 volts, and with 121 electrodes the voltage will be 24 volts, if the electrode spacing is the same in all cases. The electrode spacing in the series system, however, is closer than in the multiple system, and the voltage is correspondingly reduced.

The over-all voltage per electrode in the series system is much less than in the multiple, therefore, both on account of the closer spacing and the almost complete absence of contact resistances. The average voltage may be taken as about 20 volts per tank at a current density of 20 amp. per sq. ft.

This high voltage makes it necessary to use tanks having an insulating lining, and the lead-lined tanks used in the multiple system are not practicable. The usual construction is either of wood lined with some asphalt compound, slate, or else concrete lined with asphalt, the last being preferable, due to a longer life and cheaper maintenance.

The multiple and series systems may be roughly compared as follows: The multiple system casts heavy, thick anodes; the series requires rolled or light thin cast anodes. The multiple system requires the preparation of a special starting sheet, which is an expensive operation requiring skilled labor. The series system uses no starting sheet, but it is necessary to strip off the backs, an operation performed by common labor. The multiple system requires heavy currents per tank, necessitating heavy conductor bars with a consequent large tie-up of copper. The series system uses low currents and avoids the use of heavy conductors.

The copper produced per kilowatt-day in the multiple system at a density of 18 amp. will average about 165 to 180 lb. In the series system the production per kilowatt-day will average about 340 to 380 lb. The power requirements in the series system are thus about half those in the multiple system. The efficiency in the multiple system will average about 90 per cent, in the series system about 70 per cent, due to the current leaking past the plates. The scrap produced in the series system is less than that produced in the multiple system with a consequent less cost for re-treatment. The greater output per tank in the series system requires less tanks for any given output. The tanks used in the series system must be lined with insulating material. In the multiple system, lead linings are used. The metal losses in both systems are about equal, while the copper, silver, and gold locked up in process are less in the series than in the multiple.

Outside of the shape and arrangements of the electrodes and the tanks, the other features of electrolytic refining are common to both processes. The electrolyte has a composition of approximately 35 g. per l. copper, 140 to 200 g. per l. sulphuric acid, together with small amounts of such impurities as iron, nickel, arsenic, and antimony as may accumulate from the dissolution of the anode. The electrolyte has a marked negative temperature coefficient and, therefore, is heated by steam to increase its temperature and reduce the electrical resistance. The degree of heating used depends upon the relative cost of power and steam as well as the electrolyte composition, to a certain extent. The usual temperature is about 130°F. As the power used in overcoming the resistance of the electrolyte appears therein as heat, there is considerable heating from this source. The amount of steam used in the multiple system per tank will be greater for the same temperature than in the series system, owing to the different amounts of power developed in the tanks. A multiple tank will develop approximately 3 kw., while a series tank will develop about 10 kw.

Owing the tendency of the electrolyte to segregate under the action of the current, it becomes necessary to circulate it through the tanks. The segregation is more marked in the case of high-current densities than in low densities. It is caused by the fact that at the face of the anode, where copper is passing into solution, the electrolyte consists largely of copper sulphate of high specific gravity and there is a tendency to stream downward. At the face of the cathode, where copper is removed from the electrolyte, the latter becomes largely sulphuric acid of lighter specific gravity and the tendency is to stream upward. If, therefore, there were no circu-

lation at all, the electrolyte would soon form two distinct layers, that on top being high in acid and low in copper while the bottom layer would be high in copper and low in acid. As a result, the deposition would be largely confined to the lower part of the cathode, while there would be a copious evolution of hydrogen at the top of the cathode accompanied by spongy copper. The efficiency would, therefore, be greatly decreased, and the power per ton of copper increased. With an adequate circulation this tendency is counteracted to a large extent and the deposit kept regular. The higher the current density, the greater will be the amount of circulation required to prevent stratification. On the other hand, an increased circulation tends to keep the slime in the tank stirred up, resulting in increased metal losses. The choice, therefore, lies between greater efficiency of deposition and increased metal losses. The normal rate of circulation will be about 3 to 4 gal. per min. for current densities of 15 to 20 amp.

At some plants the electrolyte is admitted at the top of the tank and withdrawn from the bottom, while at others the flow enters at the bottom and is withdrawn at the top. The latter requires less solution, and there is less danger of a tank being flooded. This is because the solution on cooling becomes denser, and, therefore, a greater head of the hot entering solution is required to force the cooler solution from the bottom of the tank; and in case the current has been off for some time, so that the solution has become quite cool, the head required to raise the cold column of solution in the outlet pipe may be such that it is more than the tank will hold. On the other hand, the objection to the top overflow is that this type of circulation opposes the natural settling of the slime. As, however, the rate of flow per square foot of cathode surface is exceedingly small, this objection appears to be more theoretical than actual.

The older plants had their tanks arranged so that the electrolyte flowed through as many as six tanks in cascade. This practice reduced the amount of electrolyte required, but the great cooling that occurred so increased the resistance that the loss in power more than offset the reduction in the tie-up of metal in solution. The modern practice is, therefore, to reduce the number of tanks in cascade to one or two, thus preventing severe temperature inequalities and giving better efficiency and power consumption.

Circuit Resistance.—The current used in the electrolytic refining is, of course, direct current, and the amount carried by the bus bars will vary from 10,000 to 12,000 amp. for the multiple system to 500 in the series system. As the output depends upon the current, while the power depends upon the resistance, and the problem in electrolytic refining is to obtain the greatest output per unit of power, the question of resistances must be given very careful attention. The following resistances are encountered in the various systems:

Multiple.—Bus bars, bus-bar joints, anode contacts, anode, electrolyte, cathode, cathode loops, cathode-loop contacts, cathode rods, cathode-rod contacts, and other small resistances, such as resistance of the slime layer on the anode, transfer resistance, counter e.m.f., etc. The magnitude of these resistances is approximately as follows: contacts, 15 per cent; electrolyte, 60 per cent; conductors, 15 per cent; counter e.m.f., 5 per cent; slimes, etc., 5 per cent. In the series system there are the following resistances: bus bars, anode rod, anode hangers, anode, electrolyte, cathode, cathode hangers, cathode rod, and also the other small resistances mentioned in connection with the multiple system. The magnitude of the above is approximately as follows: contacts, 2½ per cent; electrolyte, 85 per cent; conductors, 2½ per cent; counter e.m.f., 5 per cent; slimes, 5 per cent. As the cost of power is one of the chief items in the refining of copper, constant thought is given to means whereby these resistances may be reduced and power saved.

Some of the ways in which savings may be made are as follows:

Conductors.—As the resistance of any conductor varies as its cross section, it is evident that any increase will result in decreased resistance. An increase in cross section, however, will increase the weight and, therefore, the cost of the conductor. Thompson's rule that the most economical cross section is that for which the interest on the investment equals the cost of power lost is applicable in this case, particularly for bus bars. For the other conductors in the tank, conditions prevent its application. Thus the anode lugs must be of sufficient strength to support the weight of the anode, and hence are usually of far greater cross section than required for the current. As the cathode loops are made of thin copper strips, these are generally of insufficient cross section and hence carry a current density greatly in excess of that which is most economical.

Contacts.—The reduction of this resistance calls for two things: (1) ample area of the contact surfaces, (2) the elimination of as many contacts as possible. This resistance is one of the largest in the tankroom, outside of that of the electrolyte, and much ingenuity has been shown in reducing it. Formerly, anodes were suspended by two hooks, giving five contacts, two at each hook, and one at the contact of the anode bar with the bus bar. The modern anode has but one contact, due to cast lugs being used which make the contact with the bus bar. Cathodes were formerly suspended by hooks which have been replaced with firmly attached loops, the attachment being below the surface of the solution, where they soon become covered with the deposit and become an integral part of the cathode An attempt has been made to eliminate the contact between the cathode rod and the triangle rod by having the cathode rod rest directly upon the anode lug in the adjacent tank.

One of the best methods of keeping contact losses at a minimum is to keep them clean. As there is generally considerable heat generated at any contact, any solution that may be splashed thereon will soon be converted into anhydrous sulphates, which prevent an effective contact. The most effective way so far developed for the prevention of this formation is to apply a thin coating of oil to the contact surfaces. This will keep them clean for a long time and costs little to apply.

While the numerical value of each contact loss appears to be so small as to be almost insignificant, it must be remembered that there are a great many of these contacts throughout the tankroom and their cumulative effect is sufficiently large to amount to a considerable waste of power.

Electrolyte.—The resistance of the electrolyte is affected by its temperature and composition. The temperature coefficient is negative, so that an increase in temperature decreases the resistance. The higher it is possible to carry the temperature, the lower will be the resistance. There is, however, a practical limitation to the degree of heating on account of the cost of the steam exceeding the saving in power beyond a certain point, depending upon local conditions. Too high a temperature may also affect the character of the deposit, and the higher the temperature, het greater the amount of evaporation and the higher the humidity in the tankroom with its attendant discomforts.

The composition of the electrolyte has a great effect on its resistance. As the conductivity is dependent on the presence of hydrogen ions, an increase in the content of acid will increase the number of hydrogen ions present and decrease the electrolyte resistance. The presence of sulphates increases the resistance. These sulphates are not only the copper sulphate composing the original solution, but also the accumulated sulphates from the impurities in the anode, such as iron, nickel, and zinc. To secure an electrolyte of minimum resistance, it is necessary to keep the free acid as high as possible and the sulphates as low as possible. The practicable limits to high acid and low sulphates are that there must be a sufficient amount of copper in the

vicinity of the cathode so that only copper ions will be discharged. This limitation, therefore, requires the copper to be kept not lower than 30 g. per l. in average work. If the acid is too high the saturation point of the sulphates present becomes very close to the operating temperature of the solution, and any cooling that may occur is likely to cause a salting out of these sulphates on the cathode, giving a very rough and contaminated deposit. The lower the contained sulphates in the solution, the higher can the acid be maintained.

Counter E.m.f.—The cause of the counter e.m.f. is largely due to the formation of concentration cells at the electrodes due to differences in the composition of the electrolyte. This may be overcome to a certain extent by increasing the rate of circulation of the electrolyte, but there is a very practical limit to this on account of the danger of stirring up the anode slime and contaminating the cathode, thereby increasing the precious metal losses and producing impure copper.

The formation of concentration cells at the surface of the cathode also causes the copper content of the electrolyte to increase, owing to the fact that, if at the top of the cathode there is a solution containing higher acid and lower copper than contained by the solution at the bottom of the cathode, a concentrate cell will be set up and copper will tend to pass into solution at the top of the cathode and be deposited at the bottom of the cathode. But as the efficiency of deposition is less than that of dissolution the copper in the solution will increase, and this amount of increase will be greater the greater the difference in solution composition.

Slimes.—The resistance of the slime adhering to the surface of the anode will depend largely on the purity of the anode. A high-grade anode produces slime that has low electrical resistance, while an impure anode gives a slime that may have a very high resistance, and should the nature of the slime be such that it covers the anode with a very heavy, dense layer, the anode may be made almost insoluble with a correspondingly great increase in the voltage necessary for the operation of the tank.

Current Density.—The current density to be used in electrolytic refining depends upon a number of factors. It is of great importance, as the design of the tankroom depends upon it. The two main factors affecting the selection of current density are the cost of power and the average composition of the anode. As the power cost varies directly as the square of the current density, a point is soon reached where the power cost becomes prohibitive. When the anode contains a large amount of silver and gold, a high current density will tend to give high metal losses in the cathode, due to the necessity of maintaining a high rate of solution circulation.

A high current density generally increases the labor cost because the weight of the cathode is more or less fixed by the physical labor of handling, and a high current density means pulling cathodes of younger age. This more frequent pulling also requires the use of a larger number of starting sheets, the preparation of which is an expensive item. The question of interest on metals locked up in process plays a very important part in the determination of current density. If the anodes are high in silver and gold, the saving due to getting these metals on the market earlier will often pay for an otherwise uneconomical current density.

Increased current density requires the use of fewer tanks and less building space for a given output. This means a lower initial investment and, where construction costs are high, may have great influence on the question.

The average current density in use at the present time will vary from 15 to 20 amp. per sq. ft. of cathode surface. In many cases this density is too high for present power costs, but as the plants were designed at a time when power was cheaper than at the present, it was correct at that time, and the only way in which the density can be reduced without building additional tanks is to curtail the output, and the loss sustained in so doing may be much greater than the loss due to increased power costs.

Current Efficiency.—The term "current efficiency" is an expression of the ratio of the amount of product actually obtained to that theoretically obtainable in accordance with Faraday's law. It is always less than unity on account of various factors, such as current leakage, short circuits in the tanks, and the deposition of hydrogen at the cathode. As the output of the tanks is directly proportional to the current efficiency obtained, other things being equal, a great deal of careful study is given to the maintenance of as high a current efficiency as is economically possible.

Current leakage in a well-designed plant should be small. It will vary with the voltage on each circuit and the care taken to keep the tank surfaces in a good, clean condition. The higher the voltage on any circuit, the greater will probably be the leakage. The amount of leakage may approximately be determined by opening the circuit in the middle and taking the ammeter reading when the voltage is normal. As this method applies the full voltage to but half the tanks, however, the indicated leakage is apt to be somewhat higher than the actual amount. Another method is to compare ammeter readings at several points in the circuit, care being taken to guard against the stray fields that exist in the neighborhood of conductors carrying heavy currents. Leakage through the woodwork of the tanks should be negligible, provided they are kept in proper condition, and it may be assumed that the largest part of the leakage is through the circulating system, by the current being shunted around the middle tanks in the circuit, as the circulating system is in parallel with the depositing system. To prevent this leakage as much as possible the resistance should be made as high as possible by having the overflow pipes of considerable length and small cross section. Where the leak occurs to the ground, there is usually evidence on account of the copper deposited at the point where the current leaves the electrolyte.

The greatest part of the loss in current efficiency is due to short circuits in the tanks. These are caused by the following conditions: the new starting sheet may curl after a few hours in the tank, and unless this is discovered and rectified a bad short circuit may result. To prevent this occurrence the starting sheets are generally removed from the tank, straightened, and replaced after a certain number of hours working. If the electrodes in the tanks are not properly aligned, there will result more or less short circuits owing to the unequal current distribution in the tank. The tank men when working on top of a tank may kick an electrode out of place and neglect to replace it properly. As the anode dissolves away, pieces of the scrap may fall off and rest against the cathode.

Except at a low current density it is not possible to produce a perfectly smooth deposit with a cathode of any considerable age, and under normal working conditions the cathodes soon become more or less rough. When this occurs the resistance between the anode and the projecting part of the cathode becomes less, and there is consequently a greater tendency for the current to flow across this part, increasing the current density at such a point and aggravating the condition. If not corrected in time, the roughness will develop into trees which bridge across the space between the anode and cathode, resulting in a dead short circuit which may stop all depositing in that particular tank. To prevent such a condition, the tank men continually patrol the tanks with voltmeters and long copper rods. When the voltmeter indicates the presence of a short circuit, the rod is swept across the space between the anode and the cathode and the projection broken off.

Deposition of hydrogen at the cathode is due to an insufficient amount of copper ions to carry the current. This condition may be caused by too low a circulation rate or by the circulation being unevenly distributed between the electrodes. It may also be caused by the copper content of the electrolyte being too low or the acid content being too high. The usual cause is probably an inefficient distribution of the circulation throughout the tank. The current efficiency may be reduced as much as 5 to 10 per cent, due to this cause.

Electrolyte Purification.—As the impurities in the anode accumulate in the electrolyte, the resistance of the latter increases, resulting in a greater power consumption, and there is also danger of the cathode being contaminated. This contamination is in addition to the contamination from adhering slime and is due to the fact that the deposited metal on the cathode is always more or less porous. This porosity permits a certain amount of the electrolyte to become entrained, and contamination from this source will not be removed by the usual washing received by the cathode prior to its charging into the wire-bar furnace. The higher the current density, the greater the tendency for porous cathodes. The addition of a small amount of glue to the electrolyte results in giving a denser deposit, but usually increases the resistance of the solution. The remedy for such contamination is to keep the electrolyte as pure as possible by constant withdrawals and replacement with fresh solution. The purification of tankroom solutions is a source of considerable expense unless the impurities have a marketable value.

The various methods of purifying the electrolyte are by the manufacture of bluestone and by the use of insoluble anode tanks with or without the recovery of the sulphuric acid.

In the manufacture of bluestone, the hot electrolyte is passed through towers containing shot copper until the free acid is brought down to about 1 per cent. The solution is then concentrated with steam coils in lead-lined tanks and sent to the crystallizing tanks where the copper sulphate is allowed to crystallize on lead strips. These crystals may be sold or else redissolved and sent back to the tankroom. The mother liquor from this crystallization contains the impurities, and if the impurity is of value, such as nickel sulphate, it may be further evaporated and the nickel sulphate crystallized out, after any traces of copper have first been removed. Otherwise the foul solution is wasted after precipitating out the remaining copper on scrap iron.

When using insoluble anodes, the solution to be purified is passed through a series of tanks containing anodes of hard lead. These tanks may be used either for the reduction of the amount of copper in the electrolyte or for the complete removal of the copper prior to the final treatment of the solution. Where it is simply desired to reduce the amount of copper in the electrolyte, the latter is circulated through the tanks at a high rate and returned to the tankroom. The high rate of circulation is desired in order that the efficiency of deposition may be as high as possible and also that the quality of the cathode produced be high enough to be sent to the wire-bar furnace. Where it is desired to remove the copper completely, the circulation is reduced. There are usually three to five tanks in series, and the copper from the first tank is generally of good enough quality to send to the wire-bar furnace. The product of the remaining tanks will, to a large extent, depend upon the composition of the electrolyte being purified. As the copper becomes depleted, arsenic and antimony are deposited as a sludge, which is generally sent to the blast furnace, if there is one at the plant, or else treated by special methods. The last tank eliminates the last traces of copper from the electrolyte. The efficiency of these tanks is very low, the average for the series being about 20 per cent or less.

If arsenic and antimony are the impurities to be eliminated, the solution is returned to the tankroom. If there is a large amount of soluble sulphates, such as iron, nickel, or zinc, the solution from the insoluble anode tanks is either sent to the sewer and the acid content wasted, or else it may be concentrated by heating to such a point that, upon cooling, the objectionable sulphates are crystallized out. The mother liquor, which is high in free acid, is then returned to the tankroom.

The use of the insoluble anode requires considerable power, but the investment required is small, whereas a large investment is required for the manufacture of bluestone. If, however, large amounts of solution are required to be purified, there is danger of depleting the electrolyte of copper to too great an extent. This is partic-

ularly true when the anode contains considerable amounts of nickel or iron, so that there is much less copper being dissolved than deposited. In such a case it becomes necessary to add copper to the electrolyte by means of bluestone or by trickling hot electrolyte through towers containing shot copper. On the other hand, with a pure anode there is a building up of the copper contents of the electrolyte, and this excess will have to be removed by one of the above methods.

The insoluble tanks are usually in two groups, the first of which has a high rate of circulation and removes the bulk of the copper, the second group removing the balance of the copper together with such arsenic and antimony as may be present. As the power consumption of insoluble anode tanks is high, an attempt has been made to eliminate the first set by utilizing the principle of the stratification of the electrolyte.[1] In this method advantage is taken of the fact that at the face of the anode there is a downward flow of the electrolyte due to the increase of copper concentration, while at the face of the cathode there is an upward flow due to the decreased copper concentration. By withdrawing the main bulk of the electrolyte from the lower part of the tank and about 10 per cent from the upper part, there is obtained from the lower outlet a solution high in copper and relatively low in acid, while from the upper outlet the solution is low in copper and relatively high in acid, the copper being less than is usually obtained from the outlet of the first group of insoluble anode tanks. As the impurities do not segregate, the solution from the upper outlet contains practically the same amount of impurities as the average solution in the tanks. This method thus saves the extra cost of one group of insoluble tanks and produces a cathode similar to those obtained from the regular refining tanks, with the expenditure of little, if any, more power than required for the production of regular cathodes.

The cathodes from the electrolytic refining, having been washed, are sent to the wire-bar furnace. This type of furnace is similar to that described under anode casting (pp. 249–251), but the operation requires more care, particularly in the poling operation and casting. Great care must be taken to have the metal at the proper heat, as cold copper will result in bars that are porous. Hot copper will absorb gases from the gases of combustion, and these gases will be liberated on cooling, giving porous copper.

Overpoling causes the surface of the bar to rise and throw out a worm, and the resulting metal will very likely be brittle. The causes of overpoling are not definitely known, but it is believed that sulphur plays an important part.

Refined copper is cast on the Walker wheel or the straight-line machine, as described previously. The Clark wheel is a modification of the Walker wheel with the molds placed radially instead of tangentially, and bars of any length can readily be cast thereon.

The commercial forms of cast copper are wire bars, cakes, slabs, ingots, and ingot bars. Wire bars are bars of approximately square cross section, the length varying from 40 to 60 in., the width and depth from 2½ to 4 in. The ends are usually tapered to facilitate admission to the rolls in the rolling mill. The weight of wire bars varies from 135 to 300 lb. according to the demands of the consumer. Cakes are square, or rectangular castings, varying in dimensions from 14 × 17 in. to 42 × 42 in. The thickness depends upon the weight desired for any particular cross section and varies from 2 to 8 in. Cakes under 28 × 28 in. are generally cast on the casting machine, the larger ones being cast in open iron split molds, placed on a copper base. Slabs are long, thin, shallow bars, usually with square ends. Ingots are small castings weighing about 20 to 25 lb. and have one or two heels cast to permit being broken up easily by the consumer. Ingot bars are bars consisting of several ingots end to end.

Cakes and wire bars are also cast vertically to reduce the amount of "set" surface.

[1] PYNE, *Trans. Am. Electrochem. Soc.*, Vol. 28, p. 111.

When casting refined shapes the molds are painted with bone ash. This gives a smoother surface than the pulverized silica used in the anode casting. For satisfactory work, the bone ash must be thoroughly calcined, be free from grease and organic matter, and must be very finely ground, 95 per cent to pass 200 mesh. It must be applied uniformly to the molds, or the excess will cause the bars to be pitted.

When casting refined copper, great care must be used. If the mold is filled too rapidly, there will be a tendency for some of the copper to run up the side of the mold and set there. Excessive vibration of the casting machine has the same effect. Unless these fins are removed by chiseling before rolling, they will be rolled into the finished rod and cause trouble. Particles of ladle lining, charcoal, etc., are known as "fish" and are removed during the casting and before the metal has set by the use of a long-handled, flat-bladed tool.

Over- and undersized bars are caused by the molds being out of level, warped, or by the carelessness of the operator in filling the molds. An oversize bar may cause trouble in the rolling mill by crowding the roll and thus producing a fin which is rolled into the product. Undersized bars cause no damage in the mill, but add to the expense of rolling owing to the shortage in weight, which requires more pieces to be rolled for the same tonnage.

As the bars set, they are sprayed with water and dumped into a water-filled bosh to cool sufficiently to permit of handling and inspecting. The inspection is very rigid, and bad-looking bars are rejected and remelted. The bars that pass the inspection are stamped with the furnace and charge number for future reference in case of complaint.

The quality of the copper is determined by assay and by taking a sample for conductivity. While the assay will show the purity of the metal, which generally is about 99.93 to 99.96 per cent, the conductivity test is relied upon to show the physical qualities. Small amounts of impurities have, in general, a very marked effect upon the conductivity of copper, and while those elements which make copper brittle do not, for the most part, affect the conductivity to any great extent, their presence will be detected in drawing the wire for conductivity purposes.

Treatment of the Anode Slime.—The anode slime contains all the silver and gold that is present in the anode, disregarding the insignificant amount lost in the cathode. It will also contain varying amounts of arsenic, antimony, selenium, tellurium, nickel, and a certain amount of copper, depending upon the degree of refining the anode.

At the tankroom the slime is generally passed over a coarse screen to remove large pieces of copper, such as anode scrap and cathode nodules, and is pumped over to the silver refinery, where it is allowed to settle in tanks of large cross section. The supernatant liquor is decanted and returned to the tankroom. The first step in the treatment is the removal of the copper content, which may vary from 15 to 50 per cent. There are several methods of accomplishing this. The earlier method was to agitate the slime with a mixture of sulphuric acid and niter in a lead-lined vat by means of mechanically rotated paddles, heat being applied by means of steam coils in the bottom of the vat. The niter oxidized the copper, which was converted into copper sulphate. When the reaction was complete, the residue was washed and allowed to settle, and the liquor decanted and sent to the tankroom. The mud was then filter-pressed and sent to the refining furnaces. A modification of this process was in agitating the mixture by means of compressed air instead of the paddles.

The serious objection to the use of this method, aside from the expense of the niter used, was in the formation of large amounts of sodium sulphate, which went back to the tankroom with the copper sulphate, and increased the resistance and specific gravity of the electrolyte. In order to avoid this and to do away with the expense

of niter, the slimes are given an air roasting with sulphuric acid present, after which they are boiled with acid to remove the copper sulphate. This method has entirely supplanted the former one.

The slime is either spread in thin layers in trays or in a thin layer on the hearth of a roasting furnace, and heated with a large excess of air to a point where oxidation occurs, but below the point where the slimes start to sinter. The slime may or may not be rabbled during the roasting, depending upon the existing facilities for catching the flue dust that is formed. When no rabbling is done, the time for the oxidation is necessarily of longer duration; a sulphuric-acid spraying may also be given. When the roast is completed, the slime is removed from the roasting furnace and conveyed in cans to the boiling tank, where it is boiled with dilute sulphuric acid, which removes the oxidized copper as copper sulphate. It frequently occurs that in this boiling a considerable amount of silver goes into solution, and this must be precipitated by the addition of the necessary amount of raw slime, the metallic copper of which reacts with the silver. The objection to this procedure is that an excess of the raw slime is generally added so that the finished slime contains more copper than is desired.

By any of the above methods the copper in the treated slime may be reduced to about 1 per cent, and the slime is then ready for the furnace treatment. The furnaces used are generally small basic-lined reverberatories, or else small basic-lined tilting furnaces, the latter being preferable on account of the smaller amount of precious metal tied up in the furnace linings, an item of no small importance. The furnaces may be fired by fuel oil, gas, or powdered coal.

The slime is charged into the furnace with a small amount of soda in order to thin out the slag formed on the melting down. The slime readily melts, and during the melting a very fusible thin slag is formed, which is drawn off as it is formed, so as to keep the surface of the slime from being blanketed and slowing down the melting. When the charge is completely molten, further additions of soda are made and the charge is oxidized by compressed air through iron pipes inserted under the surface of the charge. During this oxidation, the great bulk of the impurities are removed and the charge gradually assumes a metallic aspect. When the soda slag will remove no further impurities, the metal is covered with niter and the oxidation continued. This procedure brings the bath up to a good grade of doré, 980 to 990 silver plus gold, and the metal is then ready for casting into doré anodes. The niter slags formed during the last operation are generally charged back into the furnace with the succeeding slimes, the soda slags being sent to the blast furnace for recovery of the silver and copper content, or treated for the recovery of tellurium before resmelting. In some plants the soda slags are returned to the anode furnaces, but this practice is not to be recommended, as the various impurities in the slag enter the anode to a considerable extent, thus making them circulate in the system and usually giving trouble with the solution of the anodes in the tanks.

The doré, which is the name given to the high-grade mixture of silver and gold, is then cast into anodes by the use of a hand ladle. The anodes vary in size at the various plants, depending upon the process for removing the silver. For the average electrolytic process the size will be approximately $12 \times 6 \times \frac{1}{2}$ in. The anodes are then sent to the parting plant, where the silver and gold are separated. For this purpose there are two well-established processes in use at the present time, the sulphuric acid and the electrolytic, described in Chap. X.

Should there be platinum or palladium present in the doré, these metals will accompany the gold. The methods of extraction are chemical or electrolytic. In the former the gold mud is boiled with strong sulphuric acid and a small amount of nitric acid or niter, which dissolves practically all these metals. The resulting solution is then passed over copper to precipitate the silver and the platinum and palladium. The

resulting sludge is then dissolved in aqua regia, which dissolves the platinum and palladium but leaves the silver as silver chloride. From this solution the platinum and the palladium are recovered by the use of ammonium chloride and ignited to give a metallic sponge of a purity of 98 per cent or better.

Metal Losses in Refining.—The question of metal losses in the refining of copper, with its accompanying silver and gold, is one of great importance. The sources of losses are numerous, and vigilant attention is required to keep them within proper limits. The usual sources of losses taken in the order the material passes through the plant are as follows: weighing, sampling, assaying, anode slag, anode flue dust, cathode loss, wire-bar slag, wire-bar stack, weighing, slimes loss in silver process, gold in fine silver, silver in fine gold. There are also certain other losses, such as those from solution and theft.

In weighing, considerable loss may be experienced through lack of proper care of the scales and careless handling of test weights. In the average plant these points are generally given careful attention. A usual source of error in weighing lies in the taring of the cars carrying the incoming blister. These should be carefully tared at stated intervals and particularly after any repair work has been done on the car, no matter how slight. An error of considerable magnitude may be caused in weighing cars that are not properly protected from the wind while on the scale.

Sampling errors may easily run into large figures, and every possible precaution should be taken to see that the best practice is in use. This is particularly important where the blister copper contains considerable silver and gold. The question of moisture in blister copper is important. The average copper is very porous and will absorb up to 0.5 per cent of moisture while apparently quite dry on the surface. A frequent source of error against the refinery lies in the occluded moisture from quenching the copper as it comes from the molds at the converters. This may amount to as much as 0.25 per cent and can be determined only by carefully drying the copper at a temperature sufficient to drive off the moisture, but not sufficient to oxidize the copper.

In assaying, errors frequently occur through the laboratory using methods that give consistently low results or consistently high results. Unless the splitting limits are quite close, so that such methods are brought to the front by the frequency of umpire assays, a serious error may be introduced.

Anode and wire-bar stack losses will, to a large extent, depend upon the nature of the material being treated in the furnace. The apparent magnitude is not large judging from baghouse tests, particularly where, as is almost always the case, waste-heat boilers are installed.

Anode and wire-bar slag losses may, and frequently do, amount to a considerable item. These slags will run in the neighborhood of 40 to 50 per cent copper and must be re-treated in a blast furnace for the recovery of the copper. It is necessary to slag off the silica content, and, as the slag from the blast furnace will contain some copper, it is apparent that the more slag made in the reverberatory furnaces the more slag will be made in the blast furnace with its accompanying copper loss. This loss is particularly serious in cases where the refinery slags are treated in a black-copper furnace, as in such a case the resulting slags are very much higher in copper with a correspondingly greater copper loss to the refinery.

Cathode losses constitute one of the largest items of silver and gold losses in the process. There is always a certain amount of anode slime floating in the electrolyte and, if the cathode is rough, a large amount of this may be caught and thus pass into the wire bars, where it is lost. This loss may be controlled by careful supervision over the factors affecting the cathode deposit, such as proper refining of the anode, current density, and rate of circulation.

In the treatment of the anode slime in the silver building there is opportunity for great losses in the furnace gases. In former years these losses were of considerable magnitude, and it is only with the recent installations of the Cottrell system that their real magnitude has been appreciated. At the present time with properly designed Cottrell apparatus the losses from the silver-refinery roaster and furnace gases have been reduced to a very low point, though, even with this safeguard, careful watch must be kept on every step in the process for unsuspected leaks that, in the course of a year, may be considerable.

In the production of fine silver there is always loss of gold due to the difficulty of keeping the gold mud completely out of the silver crystals. Similarly, the refined gold always contains some silver. The partial cure for such losses is in proper care of the doré anode bags so that the loss is reduced to a minimum.

The amounts of the losses in cathodes, silver, and gold are kept continually before the management through the daily assays, so that any tendency to go wild should be promptly discovered and means taken for correction.

Losses by theft may amount to a large item, particularly if there is much small stuff such as copper scrap or scrap wire received. Such copper is easily carried out of the plant in dinner pails, clothing, etc., and a careful watch must be kept to keep this at a minimum. A thorough policy of prosecution when an employee is caught will go a great way to prevent similar occurrences in the future.

In general, it may be stated that in a well-conducted refinery the copper losses will average about 7 to 8 lb. per ton of cathodes produced. Silver and gold should break about even, provided the assays are uncorrected; if corrected, the silver loss will be about 2 per cent and the gold loss about 1 per cent of the contents of the anode, as these figures are the average corrections for the usual type of copper received by the refineries.

Properties of Refined Copper.—The melting point of pure copper is 1083°C., which may be slightly reduced by the presence of small amounts of cuprous oxide. The boiling point is in the neighborhood of 2310°C., but experimental difficulties have prevented a precise determination.

The latent heat of fusion is 43.3 cal. per g., and its specific heat varies with the temperature. The National Bureau of Standards gives the latest determination as

$$C = 0.0917 \times 0.000048(t - 25)$$

where t is the absolute temperature.

The electrical conductivity of copper varies greatly, depending upon the presence of minute quantities of various impurities. The following tables compiled from various sources, together with experimental work by the writer, show in a general way what may be expected. It must be kept in mind, however, that the presence or absence of oxygen in the copper may greatly vary the results. When the impurity is in solid solution, its effect is generally much greater than if it is in some other form. In these tables the conductivity of pure copper is arbitrarily taken at 100 per cent.

Per Cent	Conductivity, Per Cent
Aluminum:	
0.000	100.0
0.006	99.0
0.050	84.0
0.100	67.0
Antimony:	
0.000	100.0
0.020	97.5
0.050	95.0
0.100	88.0
0.250	75.0
Arsenic:	
0.000	100.0
0.005	98.5
0.010	95.5
0.050	85.0

Per Cent	Conductivity, Per Cent
0.100	75.0
0.200	60.5
0.500	40.0
Bismuth:	
0.000	100.0
0.005	100.2
0.010	99.5
0.050	98.5
Cadmium:	
0.000	100.0
0.025	99.9
0.050	99.6
0.100	99.0
0.250	97.0
0.500	96.0
Lead:	
0.000	100.0
0.050	99.5
0.100	99.0
0.300	98.5
Nickel:	
0.000	100.0
0.005	99.0
0.010	98.5
0.100	93.0
0.400	75.0
1.000	55.0
Phosphorus:	
0.000	100.0
0.005	100.5
0.020	96.0
0.070	60.0
0.150	42.0
Silver:	
0.000	100.0
0.100	99.8
0.500	97.5
1.000	95.5
Sulphur:	
0.000	100.0
0.050	99.5
0.100	98.0
0.250	97.0
Tellurium:	
0.000	100.0
0.010	100.0
0.025	99.0
0.050	99.0
0.100	98.5
Tin:	
0.000	100.0
0.050	98.0
0.100	93.0
0.500	75.0
Selenium:	
0.000	100.0
0.010	99.0
0.050	98.5
0.100	98.0
Zinc:	
0.000	100.0
0.050	98.5
0.100	96.5

The effects of the various impurities on the mechanical properties of copper may be summarized as follows:

Arsenic toughens, hardens, and increases the tensile strength of copper when present up to at least 1.5 per cent. It will not impair the forging properties when added in amounts up to 0.5 per cent and invariably improves the forging properties of impure copper.

Antimony hardens and strengthens copper, though not to the same extent as arsenic. It is not detrimental in amounts up to 0.5 per cent if other impurities are absent and the proper amount of oxygen is present.

Bismuth has by far the most deleterious effect on copper of any impurity; 0.02 per cent makes copper red-short, 0.05 per cent makes it cold-short, and 0.1 per cent makes it very brittle. The injurious effects of bismuth may, to a certain extent, be counteracted by the presence of oxygen.

Cobalt is said to confer greater durability at high temperatures and toughens, hardens, and strengthens copper in the cold.

Iron, when present in amounts in excess of 1 per cent, makes copper hard and brittle.

Lead when present alone in copper reduces the strength, ductility, and toughness of copper, as the latter has no solvent power for lead. The latter, therefore, honeycombs the structure more or less uniformly and greatly weakens it above ordinary temperatures. In the presence of oxygen and arsenic, lead may occur to some extent without ill effects. In the absence of oxygen and arsenic, 0.1 per cent lead will make copper unworkable, but with oxygen and arsenic present this amount is claimed to make copper roll better.

Nickel in small amounts—a few tenths of 1 per cent—imparts strength, toughness, and increased resistance to deformation at high temperatures. In Germany, copper containing a small amount of nickel is preferred to arsenical copper for the manufacture of fireboxs heets.

Oxygen in commercial impure wrought copper is essential where the metal has to withstand repetition of small stresses, exposure to atmosphere, influence of corrosive agents, etc. Its presence offsets the harmful effects of bismuth, lead, etc. Copper containing too much oxygen is cold-short, and, if the oxygen is in great excess, the metal is also hot-short.

Silicon, when added to copper in amounts up to 3.5 per cent, increases the hardness and assists in the production of sound castings. With 6 per cent silicon, copper is brittle. A small amount of silicon, 0.1 per cent, added to copper will increase the fluidity of molten copper so that castings free from blowholes can readily be produced.

Silver in copper benefits its mechanical properties and has no effect upon its hot-working properties.

Sulphur in copper forms a highly dangerous brittle constituent and is very detrimental to the mechanical working of copper. When present, its bad effects may, to a large degree, be counteracted by the addition of manganese or aluminum.

Oxygen-free copper (OFHC) having qualities superior to regular fire-refined copper is produced by a patented process developed by the United States Metals Refining Co. In this process the last traces of oxygen are removed in the refining process, and the metal is cast in a reducing atmosphere.

Another type of oxygen-free copper is produced by first depositing a brittle copper cathode, which is broken into pieces of the desired size. These pieces are briquetted by compressing at a pressure of 20,000 lb. per sq. in. The briquettes are then sintered in a reducing atmosphere and pass to an extrusion press, from which solid metallic copper is produced in the shapes desired.

Electric melting of copper cathodes has been developed by the International Nickel Co. This company has installed electric arc furnaces which are continuously charged with cathodes and which produce finished shapes without the usual blowing and poling operations of the refining furnaces.

CHAPTER X

REFINING OF GOLD AND SILVER BULLION

BY ELRY J. WAGOR[1]

Parting.—Gold and silver are so intimately associated in all classes of bullion produced in either mining or metallurgical operations that refining processes must not only consider the elimination of the base metals present in the alloy, but also the "parting," or separation, of the gold and silver. This separation is effected by dry, wet, or electrolytic methods.

The dry method is based on the conversion of the silver in the alloy to a chloride or a sulphide while the bullion is in a state of fusion. This principle finds application in the so-called Miller process, in which chlorine gas is passed through the molten metal, converting the silver and base metals into chlorides which pass off as fumes or are skimmed from the surface of the molten charge. The use of this method is, of course, restricted to bullion carrying limited amounts of silver.

The wet method depends upon the solubility of silver and the insolubility of gold either in nitric acid or in boiling concentrated sulphuric acid. In practice, the sulphuric acid-parting process has gradually superseded the older and more expensive nitric-parting process.

The electrolytic method is essentially a wet method, but is based on electrochemical rather than simple chemical reactions. Electrical energy is used to produce chemical changes by the passage of a current through an electrolyte. The Moebius, Balbach, and other silver-refining processes for refining bullion in which silver predominates in the alloy depend on the solubility of silver and the insolubility of gold at one electrode and a deposition of silver at the other under current action in a nitric electrolyte. The only differences in these silver-refining methods are certain mechanical variations and arrangements in the equipment used. The application of electrolytic parting to bullion in which gold is the predominant metal is found in the Wohlwill process of gold refining based on the solubility of gold and the insolubility of silver at one electrode and the deposition of gold at the other, under current action in a chloride electrolyte.

In this general outline of methods used in the parting of gold-silver alloys, detailed consideration will first be given to the Miller process, or the refining of gold bullion by the use of chlorine gas.

Miller Process of Chlorination.—The equipment and the operation of the Miller process installation in the Royal Mint at Ottawa, Canada, are described by Messrs. Cleave and Bond.[2]

This plant operates 16 chlorination, 2 tilting, and 4 ordinary furnaces. The chlorination furnaces are of fire clay, cylindrical in shape, with an inside diameter of 9 in. and a depth of 18 in. This battery of furnaces is connected with a large flue chamber provided with a spraying system for washing and cooling the fumes developed in the operation of chlorination. Provision is made for the recovery of values in the water through which the fumes have passed in a series of filters and settling tanks. Chlorine gas is supplied from cylinders housed in a brick leakproof closet. The gas is

[1] Superintendent, Melting and Refining Department, U. S. Mint, Denver, Colo.

[2] *Eng. Mining Jour.-Press*, Feb. 3, 1923.

conducted through a heavy lead pipe extending along the top of the flue chamber with a branch leading to each furnace fitted with a valve for regulating the flow of gas to the different units.

Clay crucibles are used having a height of 11¼ in. and a diameter at the top of 5¾ in., tapering to 3¼ in. at the bottom. These are provided with slotted covers to allow inserting and withdrawing the clay pipe stems, which are about 2 ft. in length and $\frac{3}{16}$ in. in diameter. In the operation of chlorination, the clay crucibles are placed inside graphite crucibles as a safeguard against leakage or breakage.

Bullion for treatment is first melted in a tilting furnace in charges of 7000 to 8000 oz. After the chlorination equipment is brought to a red heat, 600 to 700 oz. of the molten bullion from the tilter is poured into each crucible, sufficient borax having been previously added to form a cover ¾ in. in thickness. The pipe stems are forced to the bottom of the crucibles and held in position by clamps. The gas is turned on slowly at first, and the flow is gradually increased to the maximum where no free chlorine is given off. The base metals are immediately attacked, and pass off in dense fúmes, which are drawn into the chamber through the furnace flues.

After the base metals have been practically eliminated, chloride of silver is formed, which floats on the surface of the gold beneath the borax cover. When chlorination has been completed, determined by a brownish stain formed on a clay rod held in the fumes, the remaining silver chloride and other impurities are baled off. The gold is then cleaned up with bone ash and poured into a mold, and the crucible is ready for another charge.

The time necessary for the completion of the operation depends, of course, on the amount of silver and base present in the bullion. Bullion containing 800 parts gold, 150 parts silver, and 50 parts base metal per 1000 requires 1¾ hr. for chlorination, and during this period it is necessary to skim off the silver chloride formed three times to prevent it from overflowing the crucible.

The chlorides skimmed off during the operation are remelted in a No. 45 graphite crucible, and sodium carbonate is slowly charged in on the top of the melt. This effects a partial reduction of the chloride to metallic silver, which, in settling to the bottom of the crucible, carries with it the gold contained in the chloride. The charge is allowed to cool sufficiently to solidify the metal, and the still molten chloride is poured into shallow molds. The silver containing the gold is cast into anodes and refined by the electrolytic Moebius process.

The chloride cakes are treated in a tank with boiling water to remove the base chlorides, and then placed in another tank in alternate layers with iron plates for reduction of the chloride to metallic silver. This silver will sometimes approximate a fineness of 999. The gold from this process will average 996.5. With a plant as outlined, it is possible to produce 250,000 oz. of refined gold in a 48-hr. week.

Sulphuric Acid Parting.—This process has been described in detail by Schnabel in his "Handbook of Metallurgy," by T. K. Rose in "The Metallurgy of Gold," and by others, and consists essentially in four operations as follows: (1) blending of the bullion to required fineness and preparation for parting operation; (2) dissolving of the silver by sulphuric acid; (3) treatment of the residues for gold; (4) recovery of the silver from sulphate solution.

Blending of the Bullion.—The bullion must be blended or mixed in such proportion that a melt of prescribed weight must contain certain definite proportions of gold, silver, and base metals. The make-up varies in different plants, ranging from 2⅛ to 4 parts of silver to 1 part of gold according to the amount of copper present. The sulphates of the base metals present in the bullion are only slightly soluble in concentrated sulphuric acid, and care must be exercised in keeping the base-metal content within certain limits. The copper present should never exceed 10 per cent, and, if

possible, should be kept under 6 per cent. Lead, up to 5 per cent, does not materially interfere with the process. The bullion is melted in graphite crucibles in melts of 3600 to 6000 troy oz.

In order to expose the maximum amount of surface to the action of the acid, these melts are either granulated or poured into thin slabs. Granulations are made by pouring the molten metal, in a small stream with a whirling motion, into large copper tanks filled with cold water. After pouring, the water is drawn off and the granulations are dried on heated trays of either copper or iron. Slabs for parting are cast into shallow iron molds ¾ in. deep by 9 in. wide by 15 in. long. The advantage claimed for the slabs over granulations is in the less violent action of the acid, thus affording better control of the dissolving action.

Solution of the Silver.—This is effected in cast-iron pots of fine-grained, compact white iron containing a small percentage of phosphorus or silicon. These pots are usually hemispherical in shape, 40 in. or less in diameter, with a 1½- to 2-in. wall. Covers, either of cast iron or heavy sheet lead reinforced with iron, are fitted to the pots with lead-pipe connection for carrying off the fumes of sulphur dioxide and openings for charging with metal and acid. Dissolving kettles have capacities ranging from 3600 to 16,000 troy oz.

For each part of silver in the bullion, 2 to 2½ parts by weight of commercial concentrated sulphuric acid, 66°Bé., is added. Heat to facilitate action of the acid is usually applied by wood fire, and extreme care must be used in regulation of the temperature in controlling the ebullition. One-half of the total acid required is added at the start, and the remainder from time to time as the action warrants. During action, the charge must be stirred occasionally with an iron tool. The time required for complete solution of the silver varies from 6 to 12 hr., depending on the amount of base metal present and the care with which repeated stirrings are made. The acid vapors are led to a condensing chamber where particles of silver sulphate carried over may be deposited. SO_2 may be recovered in leaden chambers as sulphuric acid, ferrous sulphate, or hyposulphite.

The reaction represented in the process would be

$$Ag_2 + 2H_2SO_4 = AgSO_4 + SO_2 + 2H_2O$$

The base sulphates are only slightly soluble and, therefore, have a tendency to stay with the gold residues; their chemical reactions are, as a rule, quite complex. In the end, a small amount of cold acid is added to help clear the solution. The clear solution of silver is ladled or siphoned into lead-lined tanks partly filled with hot water, in which the precipitation of the silver is effected.

Treatment of the Residues for Gold.—Repeated boilings of the gold residues with fresh concentrated acid are necessary to remove the remaining silver and base metal. Often as many as seven boilings are necessary. Residues are finally washed with hot water or hot dilute acid to remove the anhydrous sulphates. The gold is pressed, dried, and melted with a flux of niter and bone ash, and is cast into bars having an average fineness of 995.

Recovery of Silver from Sulphate Solution.—Silver may be recovered from solution by precipitation with copper, iron, or ferrous sulphate. The most common method is by copper replacement, in which the solution is brought to a concentration of 24°Bé. by steam, and silver is precipitated as cement silver on scrap copper placed around the sides and on the bottom of the tank, or, better, on slabs of copper hung vertically in the solution. After the silver is completely precipitated, it is allowed to settle and the clear solution siphoned off. The silver is removed to a wooden filter tank where it is thoroughly washed. After pressing into cakes, it is dried and melted,

giving a product, after fluxing, 990 to 998 fine. Further refinement, if necessary, may be accomplished by cupellation.

In the iron method of recovery, the silver sulphate is separated out in solid form and packed in layers alternating with layers of sheet iron. This method is attended with much heat and considerable gassing, but is more economical. The silver may also

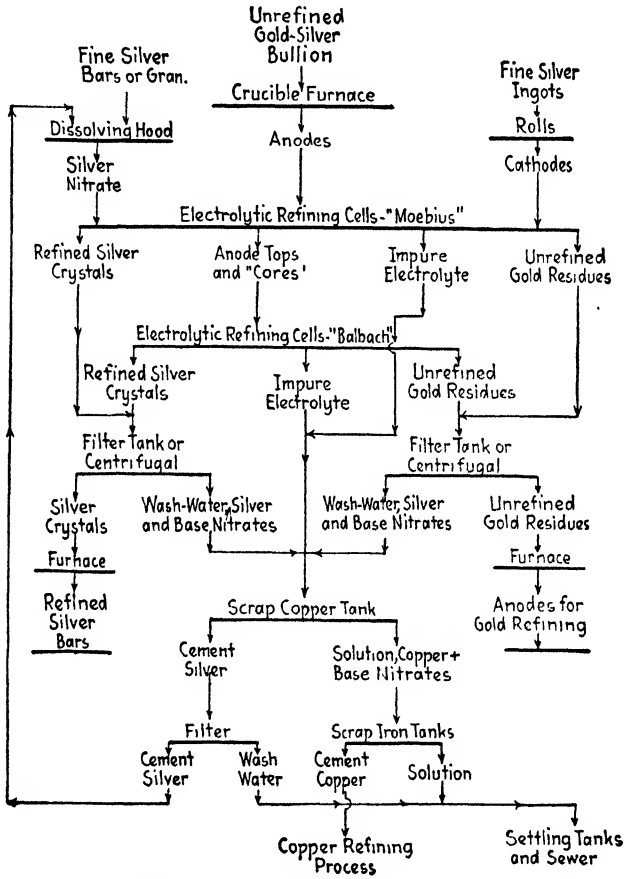


DIAGRAM 1.—Silver refinery flow sheet.

be recovered by running a hot solution of fe. ›us sulphate through a filter containing crystals of sulphate of silver according to the reaction

$$Ag_2SO_4 + 2FeSO_4 = Ag_2 + Fe_2(SO_4)_3$$

The ferric sulphate may be reduced by iron and used again for reduction of the silver.

Where copper is used for precipitating the silver, the copper in the mother liquor may be crystallized as copper sulphate by alternate evaporation and crystallization on lead sheets suspended in lead-lined tanks.

Electrolytic Processes.—Electrolytic methods of refining have, to a large extent, replaced or supplemented the acid-parting process not only in large-scale operations but also in the smaller plants, in private as well as government-operated refineries. The advantages over acid parting may be summed up as follows: (1) lower cost of

operation, (2) higher standard of refined product, (3) neatness of operation and absence of noxious fumes, (4) recovery of the platinum metals as by-products.

The Moebius and Balbach systems of silver refining find application in the treatment of bullion ranging from a few points of gold (doré silver) up to 350 parts per 1000; the Wohlwill process of gold refining, in the treatment of bullion containing 850 or better of gold per 1000.

The Moebius Process.[1]—Wooden tanks of pitch pine may be used, thoroughly tarred to prevent leakage. These tanks, 2 ft. wide by 12 ft. long, are divided by transverse wooden partitions into seven compartments or units. In each compart-

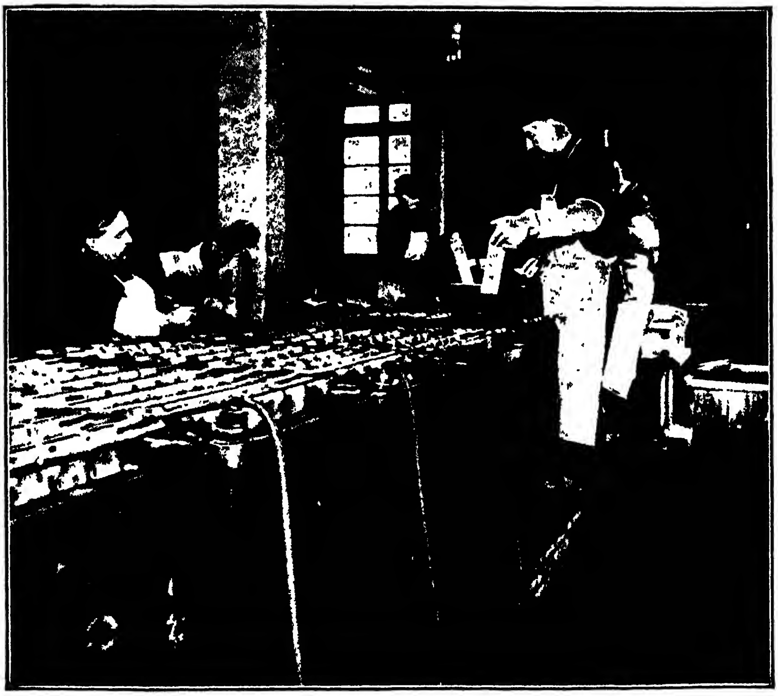


FIG 1.—Moebius cells. Anode shown at left. Stripping cathode at right.

ment are suspended three rows of anodes and four rows of cathodes. The anodes are suspended in muslin bags or cloth frames which serve to collect the undissolved metals and prevent contamination of the deposited silver. The cathodes are thin rolled strips of pure silver, which are straddled by mechanically operated wooden scrapers removing silver crystals as fast as they are deposited, and serving to keep the electrolyte uniform by gentle agitation. A removable tray is placed under the electrodes for removal of the silver, and all arrangements, electrodes, scrapers, etc., in each unit are carried on a frame and can be lifted together from the refining tank.

The electrolyte is a weak solution of silver nitrate containing free nitric acid, though the operations may be started with a dilute solution of nitric acid.

In the treatment of doré silver bullion the permissible current density varies from 20 to 28 amp. per sq. ft. of cathode surface, and the potential across the electrodes, or of the unit, is 1.4 to 1.5 volts. At this density about 40 per cent of the daily output

[1] For a description of this process as practiced at Maurer, N. J., see Griswold, *Eng. Mining Jour.*, Vol. 107, p. 789, May 3, 1919.

of each unit is permanently held in stock in cathodes and electrolyte. The energy consumption is 13.2 watt-hr. per oz. of silver deposited.

The anode mud, consisting of gold, some silver, lead as peroxide, and other insoluble metals, is removed periodically from the bags and, after washing, is parted by acid or other means.

The silver is deposited in a loose crystalline form easily removed from the cathode, although at lower current densities it is deposited in a more adherent form. An addition agent, as gelatin or glue in the electrolyte, to harden the deposit, is effective only when the solution is comparatively free from base metals.

Balbach Process.[1]—The electrolyte used in this process is the same as used in the Moebius, but the anodes, instead of being suspended vertically in the electrolyte, are placed horizontally in filter frames or baskets supported on the edges of the tanks, and the silver is deposited on a cathode fitted to the bottom of the refining cell or tank. Originally, this cathode was made of silver, but the universal practice now is to use graphite plates, ½ in. thick, cut to size to fit the bottom of the refining tank. Contact with these plates is effected by use of silver candle-shaped contact pieces cast in a special mold, and in a similar manner electrical connection is made with the anode. The anodes are cast in thin slabs and placed in the muslin-lined wooden frames or baskets with grill bottom. The insoluble residues accumulate on the underside of the slabs as the parting progresses, thus gradually increasing the resistance of the cell. The deposited silver is removed from the bottom of the cell by a long-handled scoop of wood or hard rubber, the anode basket being raised clear of the cell to facilitate the operation.

The distance between the electrodes is 4 in. and the depositing surface about 8 sq. ft. With a voltage of 3.8 per tank and a current density of 20 to 25 amp. per sq. ft., the energy consumption is 31.5 watt.-hr. per oz. of silver produced, and 32 per cent (approximately) of the daily output is held in process in electrolyte and contact pieces. No agitation or circulation of the electrolyte is required in this process.

A critical comparison of the Moebius and Balbach systems is made by F. D. Easterbrook.[2] It is to be noted that the Balbach cell is simpler in its operation, having no moving parts. Its energy consumption, however, is greater, and its depositing surface per unit of floor area is considerably less than that of the Moebius.

An innovation in silver refining was tried for some time in the Ottawa Mint in Canada, and was described by A. H. W. Cleave.[3]

The cell made use of a rotating cathode and permitted a current density of 150 amp. per sq. ft. of cathode surface at a voltage of 2.5 without unduly increasing the temperature of the electrolyte. These cells were 36 in. in diameter, and the electrolyte was contained in the annular space 8 in. wide by 18 in. deep between the outer and inner walls of the cell. The cathode carrier was supported at the center of the cell and was revolved by a shaft passing through this central hollow space. The deposited silver was loosely adherent and was automatically scraped from the cathodes, falling into removable trays from which the silver was removed every 4 hr.

An interesting comparison between the Moebius and the newer type of cell was given by Cleave.[4] In spite of the apparent advantages, it is understood the newer cell was abandoned.

The United States government in its Mint and Assay Service operates three electrolytic refineries. All classes of bullion are received for refining, except that in which

[1] Balbach Refinery, *Elec. Chem. Ind.*, Vol. 2, p. 302; THUM and EASTERBROOK, *Electro. Chem. Met. Ind.*, Vol. 6.

[2] *Trans. Am. Electrochem. Soc.*, Vol. 8, p. 125.

[3] *Eng. Mining Jour.-Press*, Vol. 116, p. 21.

[4] *Loc. cit.*

the base-metal content exceeds 800 parts per 1000, and electrolytic processes are used exclusively in the parting and refining operations, the Moebius and Balbach-Thum processes for silver, and the Wohlwill method for gold. Most of the refined silver is produced by the Moebius or "vertical system," the Balbach-Thum or "flat cells" being used to supplement the Moebius-cell operation in treatment of the unparted anode remnants and bullion too base to be handled by the "vertical system."

The cells used in the "vertical system" are of vitrified acidproof stoneware, either of earthenware or domestic porcelain, 44 to 48 in. long, 24 in. wide, and 18 to 24 in. deep. The electrode supports are either hard-rubber rods reinforced by a steel core, or close-grained maple sticks, rounded on one side and painted with an acidproof paint. Half-round conducting strips of either gold or silver cover the top sides of the electrode supports and are fastened to bus bars placed along the edge of the cells. The distance between electrodes varies from $2\frac{1}{2}$ to 3 in. The anodes are cast with a hole in the top and are suspended in muslin bags from the conducting supports by C-shaped hooks of gold. The cathodes are strips of silver rolled out to a thickness of $\frac{1}{16}$ in. and bent over at one end to hang from the supports.

The electrolyte is a 3 per cent solution of silver nitrate containing about 2 per cent of free nitric acid. It is kept uniform either by circulation effected by air lifts of hard rubber, forcing the solution from the bottom of the cell and discharging at the surface, or by gentle agitation furnished by glass propellers connected to a motor-driven line shaft.

The first step in the operation is the preparation of the bullion for refining, the making of anodes for the refining cells. While the process allows considerable latitude in the amount of gold in the anode, it is customary in practice, in order to secure more uniform conditions in the cells, to make up anodes having a definite ratio of gold to silver. The usual make-up is an alloy containing 300 to 350 parts of gold per 1000 with not over 100 to 150 parts of base produced by blending low-grade gold bullion, which cannot be handled directly by the Wohlwill process, with bullion in which the silver predominates. These silver anode melts of 4500 to 4800 troy oz. are melted in No. 100 graphite crucibles and cast into anodes of the desired shape and size. A tapering pin in the mold provides the hole in the anode used for suspension in the cell.

A current density of about 14 amp. per sq. ft. of cathode is maintained, using a voltage of 1 to 1.3. Under current action, the silver and base metals are dissolved at the anode, the gold and insoluble residues remaining in the muslin bag in a brittle brownish-black condition resembling a poor grade of lignite. This "black gold," as it is called, retains the original shape of the anode, and when removed from the cells it is broken up to remove "cores" of unparted bullion which it sometimes contains. After a thorough washing with hot water, the black gold is dried and melted into anodes for treatment by the Wohlwill process. The fineness of these anodes depends not only on the quality of silver anodes from which obtained, but also on the current density used in the parting operation and the condition of the electrolyte. The fineness ranges from 800 to 900 parts of gold with 50 to 100 parts of silver.

Pure silver is deposited on the cathodes in a crystalline form; this is scraped from the cathodes at intervals into porcelain jars. Crystals that fall to the bottom of the refining cells are periodically removed and added to the cathode production. The collected silver is thoroughly washed with hot water, in either porcelain filters or earthenware centrifugal machines. In the latter case, the silver is placed in an earthenware basket or rotor, lined with 7-oz. cotton duck, provided with a series of channels at its periphery for carrying off the wash water. This basket makes 800 r.p.m., and washing is effected very rapidly. After washing, the centrifugal is operated for a time, drying the silver sufficiently to be removed and charged into the

crucible for melting. If washing is done in an ordinary filter, provision is sometimes made for drying the silver crystals in a steam drying oven. The silver is melted in No. 100 to 125 graphite crucibles in melts of 5000 to 5500 troy oz. without the use of fluxes, and cast into bars having an average fineness of 999.5. A cast-iron cover, placed over the mold after pouring, prevents "spitting" of the silver in cooling.

There is a gradual depletion of silver and acid in the electrolyte as the base metals pass into solution at the anode, and this must be taken care of by additions of strong silver nitrate and nitric acid. The electrolyte is tested at intervals to determine the extent of this depletion. Titrations are made with potassium thiocyanate, using ferric sulphate as an indicator for silver determinations, the acid being determined by potassium hydroxide, with methyl orange as an indicator.

The "flat cells" of the Balbach-Thum process, used to work up the cores or unparted remnants of the bullion from the vertical cells, are of brown earthenware 39 in. long, 19 in. wide, and 12 in. deep. The tray or basket, in which is placed the unrefined bullion, is either of earthenware or of wood. If wooden baskets are used, no metal should be used in their construction. Several thicknesses of filter cloth are needed in the basket, as the parting is attended with considerable heat. Connection is made to the anode by a candle made up of a 50 per cent gold and 50 per cent silver alloy, which easily withstands the action of the current, and to the carbon plates or cathodes by long candles of fine silver. Copper lugs are fastened to the tops of these candles for connection with the conducting cables. The distance between electrodes is about 6 in., and the depositing surface is 5 sq. ft. The resistance of this cell is high, requiring a potential of 5 volts to maintain a current density of 14 amp. per sq. ft. No agitation or circulation of the electrolyte is needed.

The operation of these cells is similar to that in the vertical cells. The silver is removed by long-handled scoops of rubber or wood and added to the production of the other process, and the "black gold" from the baskets is washed and melted into anodes for the gold cells. Three or four of these cells will take care of the cores from 16 vertical cells.

The electrolyte becomes foul in time and is drawn off, and the silver in this solution, together with the wash waters from the fine silver and black gold, is recovered by precipitation on copper scrap as cement silver. This recovered silver may be used in the making of strong silver nitrate for additions to the refining cells or in the make-up of silver anodes.

A flow sheet of the silver-refining process (Diagram 1) outlines the general procedure in the government refineries.

Wohlwill Process of Gold Refining.—The cells are of white Royal Berlin porcelain, 16 in. long by 11½ in. wide by 12 in. deep, inside, usually arranged in batteries of 12 to 15 cells connected in series. One plant is successfully using cells of domestic porcelain 44 in. long, 24 in. wide, and 18 in. deep. Electrode supports are of porcelain or hard-rubber, steel-reinforced rods, or, where the larger cells are used, maple sticks painted with acidproof preparation are used. As in the silver system, these supports are covered with strips of gold for conducting the current. The anodes are cast with a hole in the top and suspended from the anode supports by C-shaped gold hangers or hooks. They are cast in a shape to minimize the amount of scrap to be re-treated, as shown in Fig. 3.

While anode *C* seems to offer the smallest percentage of scrap for remelting, a larger percentage of the anodes were broken when casting, as the metal is often quite brittle. At best, about 10 per cent of the metal treated in the cells is returned for remelting in the form of anode tops. The tapering of the anode in its thickness permits of more uniform corrosion in the cell, the strongest action being at the solution line.

The cathodes are strips of fine gold rolled out to a thickness of 0.01 in. and cut to proper length. One end is turned over to permit of hanging from the cathode support. These starting sheets are annealed to prevent warping or buckling in the cell, care being used not to soften the turnover which supports the weight of the deposited gold.

The electrolyte is a solution of gold chloride containing 50 to 60 g. to the liter of gold, with 5 to 7 per cent of free hydrochloric acid. It is kept uniform in the same manner as the silver cells, by circulation, by using an air pump, or by agitation furnished by glass propellers.

The current used is a pulsating or nonsymmetrical alternating one, obtained by connecting a direct-current generator in series with an alternating-current source, which source may be either an alternating-current generator of proper voltage, or a high-voltage source stepped down by use of an induction regulator. The refining can be done by direct current alone, but the pulsating current makes possible the

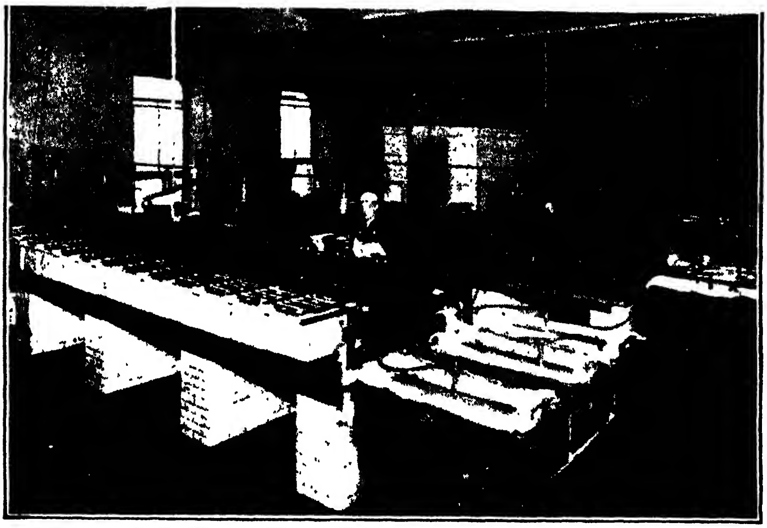


FIG. 2.—Wohlwill cells with glass-propeller agitation (foreground); Moebius cells (center); Thum-Balbach cells with candle connections (right).

refining of gold bullion containing a higher percentage of silver at higher current densities and with less free acid. This current, its application and advantages, are described by the inventor, Dr. Emil Wohlwill.[1] The electrodes do not change polarity unless the alternating current is greater than $\sqrt{1.5}$ times the direct current (*Z. Electrochem.*, Vol. 49, p. 471, 1943).

In each cell there are three anode and four cathode supports. Three cathodes are suspended from each support, giving a total depositing surface of 2.8 sq. ft. per cell. The depositing surface in the large cells mentioned is 10 sq. ft. The current density used is 50 to 70 amp. per sq. ft. of cathode surface at 0.8 to 1.1 volts per cell, and the ratio of alternating to direct current is determined by the silver content of the anode.

Under current action, the anodes that contain 8 to 10 per cent of silver are dissolved, the gold as well as the platinum metals together with the base passing into solution, while the silver is changed to insoluble chloride and falls to the bottom of the cells. Osmiridium crystals in the anode are not affected by the current and fall with the silver chloride. An excess of silver in the anodes forms a coating of chloride,

[1] *Met. Chem. Eng.*, Vol. 8, February, 1910.

which protects them from further action, thus rendering them practically insoluble, and an evolution of chlorine results.

The gold deposited at the cathode is very hard and quite dense, and the starting sheet is melted with the deposited gold. The cathodes are removed after receiving

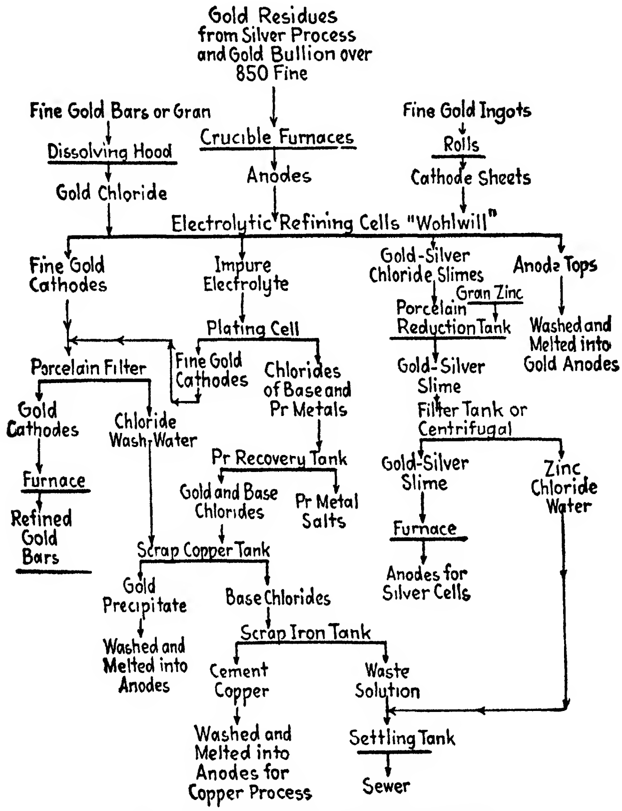


Diagram 2.—Gold refinery flow sheet.

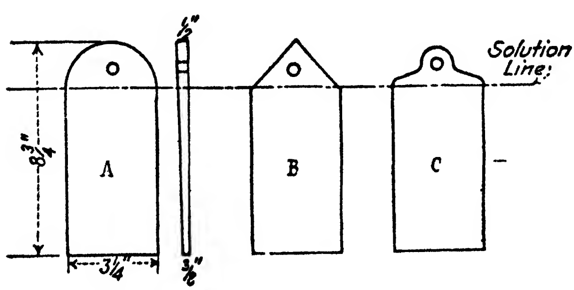


Fig. 3.—Anode types.

a deposit of 150 to 200 oz. of gold, washed in porcelain filters, dried, and melted without the use of fluxes in melts of 8000 to 9000 oz. and cast into bars having an average fineness of 999.5 to 999.8. Frequently, these melts will run to 999.9 in fineness.

FIG. 4.—Motor-driven earthenware centrifugal for washing and drying slimes.

FIG. 5.—Wohlwill cells. Anode shown on left, cathode on right, thin rolled gold strips in foreground for starting sheets.

As the base metals are dissolved at the anode, the gold content of the electrolyte drops and it is necessary to add strong gold chloride at intervals. A rapid and fairly accurate method of testing the electrolyte is to precipitate the gold in 1 cc. with an excess of ferrous ammonium sulphate, and to determine the excess used by titrating back with potassium permanganate. The ferrous solution is prepared by dissolving 154 g. of the salt in 500 cc. of distilled water, adding 5 cc. of concentrated sulphuric acid and diluting to 1 l.; 1 cc. of this solution will precipitate 25 mg. of gold. The permanganate solution is made up so that 1 cc. will equal 1 cc. of the ferrous solution by dissolving 12.3 g. of the salt in 1 l. of distilled water.

In order to take care of the depletion of gold in the electrolyte, it is necessary to keep constantly on hand a stock of strong gold chloride. This chloride is made either by dissolving fine gold bars or granulations in aqua regia, or electrolytically, by passing a current through an electrolyte of concentrated hydrochloric acid, using anodes of fine gold and fine gold cathodes suspended in a porous porcelain cell. The porous cup prevents the deposition of the gold at the cathode, and the gold dissolved at the anode is retained in solution. In either method, the operation is carried on under a hood. The resultant gold chloride has a strength of 375 to 450 g. of gold per liter.

About 5 per cent of the gold treated falls mechanically into the silver chloride slimes. The reduction of the silver chloride is effected by use of granulated zinc in porcelain tanks, sufficient acid being present to start the action. After reduction is complete, the slimes are thoroughly washed in a filter or centrifugal machine and melted directly into anodes for the silver-refining cells. These slimes will average in fineness 250 to 500 parts gold, 30 to 40 parts base, balance silver, and in the melting, sufficient gold or silver bullion is added as required to produce an alloy of the fineness required by the silver-refining operations.

The gold in the spent electrolyte and wash waters is recovered by precipitation with ferrous sulphate or by scrap copper. As gold so recovered is in a very fine state of division and difficult to melt and wash without loss, an electrolytic recovery is to be preferred. This is accomplished by the use of a double-compartment cell in which a small cell is placed in the center of a large cell. The inner cell is charged with concentrated hydrochloric acid, while the foul electrolyte is placed in the outer cell, and connection is made between the two solutions by a series of short glass siphons resting on the edge of the inner cell. The air is exhausted from these siphons, and the solutions enter, thus permitting a flow of current through the electrolyte. Anodes of fine gold are suspended in the inner cell and gold strips in the outer cell. Under current action, gold chloride is formed in the inner compartment and the gold in the spent electrolyte is deposited on the cathodes. By regulation of the voltage, practically all the gold in the foul electrolyte may be plated out and the gold so obtained forms parts of the regular production of the cells. One or two of these plating cells will handle all the foul electrolyte from 48 of the small refining cells and at the same time add considerably to the stock of strong gold chloride.

As the government has no interest charges to consider on metal held in process, the noble metals are used for conductors, and the problem of securing good electrical contacts is in a measure eliminated.

A flow sheet (Diagram 2) shows the procedure in gold-refining operations.

All the foul solution from which the silver and gold have been recovered is upmped into large wooden tanks containing scrap iron, in which the copper is recovered as cement copper, and any gold, silver, or platinum metals that have escaped the previous operations are recovered. To recover the values in this cement copper, a small electrolytic copper plant is operated, producing pure copper and a sludge containing the precious metals. This sludge is a veritable dragnet of impurities, containing

besides Au, Ag, and Pt, the base metals Cu, As, Sb, Pb, Bi, etc. This is usually handled in small amounts in silver-anode melts and the precious metals recovered from the regular process.

Platinum Metals Recovery.—The procedure for the recovery of the platinum metals in the government refineries is as follows:

The foul electrolyte from the gold-refining cells is allowed to cool, thereby permitting the salts of silver and lead to settle. The clear solution is siphoned off, ammonium chloride is added with thorough stirring, and the yellow ammonium chloroplatinate is precipitated. After the platinum salt has settled, the solution is transferred to a stoneware tank for the recovery of palladium.

This solution is electrolyzed, using an insoluble carbon anode and a refined gold sheet as the cathode. Under current action, chlorine is evolved at the anode and a flesh-colored salt of palladium is formed which settles to the bottom of the cell while the gold is deposited in a pure state at the cathode. The current during this operation is gradually reduced as the gold in solution becomes depleted in order to keep the gold deposit hard and prevent contamination of the palladium salt. The range of current density is 20 amp. to 2 amp. per sq. ft. of cathode surface. The electrodes are spaced 2½ to 4 in. apart. The deposited gold is added to the gold-cell production, while the gold remaining in the electrolyte is recovered by cementation on copper slabs. The remaining solution finds its way to wooden tanks where copper and traces of the precious metals are recovered by cementation on scrap iron.

The platinum and palladium salts are washed with a cold saturated solution of ammonium chloride and dried. The palladium is very soluble, and great care should be exercised in the washing; the ammonium chloride should be freshly chlorinated, and only the bulk of the gold and copper chloride should be removed.

Iridium is recovered from the iron skimmed from certain melts. These skimmings are granulated and dissolved in hydrochloric acid to remove the iron. Further treatment of the residues is necessary depending on the metals present before using the usual peroxide fusion for recovery of the iridium. Crystals of osmiridium may be recovered directly in the gold-refining cells.

Platinum Metals Refining.—Practically all the refining and melting of the platinum metals is performed at the United States Assay Office in New York.

The usual procedure in refining crude platinum sponge is to redissolve in aqua regia, evaporate the solution to dryness to expel the nitric acid, dissolve the residue in water, and reprecipitate the platinum with ammonium chloride. In large-scale operations, this is a long and tedious process, so the government refineries have developed an electrolytic method to effect a solution of the crude sponge.

The crude sponge is placed in perforated stoneware cells or baskets that are suspended from the electrode support in an electrolyte of hydrochloric acid, contact being made by a heavy platinum strip fastened to the bus bar and penetrating the sponge. The cathodes are thin platinum sheets suspended from heavy platinum-wire conductors in porous cells of the same size and shape as the perforated anode basket. The electrolytic action dissolves the sponge at the anode, while the porous cup prevents the deposition of the dissolved platinum at the cathode. An alternate scheme, which also gives satisfactory results, is one in which a platinum sheet is placed on the bottom of the electrolytic cell, the crude sponge is placed on this sheet as the anode, and the porous cups in which are the platinum strips are placed at the ends of the cell. Air is used for agitation of the electrolyte. This solution from the crude sponge is evaporated on steam coils to remove excess acid, and filtered and ferrous sulphate is added to remove the gold. The solution is carefully filtered again and the platinum again precipitated with ammonium chloride. This precipitate should be freed from the filtrate as soon as possible and washed until free of iron. The platinum salt is

dried and reduced to sponge by gentle heating in a clay crucible. The refining is carried on in batches of 1000 to 2000 troy oz., and the crude sponge can be raised from 80 per cent to 99½ per cent in one treatment as outlined.

The crude red salt of palladium, after washing, is treated with ammonium hydroxide until no more is dissolved, and after filtering, the yellow dichlorodiammine palladium is precipitated by cautiously adding hydrochloric acid until no more of the yellow salt forms. During this precipitation, great care must be exercised to prevent overheating, and an excess of acid should be avoided. This yellow salt is drained, washed, and redissolved with ammonium hydroxide and again precipitated with hydrochloric acid. It is then carefully washed on a filter, dried, and sponged in clay crucibles. This sponge is ground and reduced by soaking in alcohol and bringing to a red heat in a carbon or graphite crucible fitted with a tight cover. This sponge must be allowed to cool in the crucible. Palladium having a purity of 99 to 99.75 per cent results.

An Ajax-Northrop induction furnace is used in the melting of the platinum and palladium sponge, using a specially designed zirconium-oxide crucible. Due to the high temperature and the thorough mixing action afforded by the induction furnace, the metal is considerably better for spinning than when melted by the torch method.

An excellent treatise on the purification of the platinum metals is furnished by Edward Wichers, Raleigh Gilchrist, and William Swanger.[1] Further notes on the treatment of the platinum metals will be found in the last chapter, Minor and Rare Metals.

[1] *A.I.M.M.E. Tech. Bull.* No. 87, March, 1928.

CHAPTER XI

HYDROMETALLURGY OF GOLD AND SILVER[1]

Occurrence of Gold.—Native gold is invariably alloyed with more or less silver, but it is exceptional to find any other metal in the alloy. It is found in veins associated with quartz and various sulphides—notably pyrite, pyrrhotite, galena, chalcopyrite, arsenopyrite, less commonly blende; sometimes with carbonates, especially ankerite; and small proportions of tellurides of lead and bismuth. Sometimes the metal is finely disseminated through such sulphides, sometimes deposited on the surface of the mineral particles in fairly large grains. One particular sulphide, *e.g.*, chalcopyrite, may monopolize the gold. In the oxidized portions of veins the gold is often associated with limonite, and gold-bearing quartz often contains small proportions of copper carbonates and manganese oxides. Electrum, containing 35 per cent or more silver, is found only in the vicinity of silver mines. When gold is found apparently disseminated in igneous or metamorphic rocks, minute veinlets of quartz or carbonate usually accompany it.

Gold telluride, usually containing silver and sometimes mercury telluride, occurs in veins of quartz and carbonate; when oxidized, the resulting native gold is often extremely pure and finely divided and may be coated with tellurous oxide (mustard gold).

The gold of placers or creek and river gravels is found occasionally in nuggets of large size, but more commonly in small grains, often water-worn; in some deposits a considerable proportion of the grains pass a 200-mesh sieve. The silver content averages less than in vein gold, and it is, as a rule, easy to amalgamate. That from buried river gravels is similar, but often coated with oxide or sulphide of iron. The gold of sea beaches is usually finely divided or in thin scales.

For metallurgical purposes gold has been roughly classified as "free" or amalgamable and "refractory"; "float gold" is fine and in a condition making it easily floatable on water—the telluride is also easily floated—"rusty gold" is coated with some mineral that retards amalgamation (usually oxide of iron, manganese, or tellurium); "encased gold" is completely enveloped in grains of quartz or other mineral and requires finer crushing to liberate it.

Among the minerals sometimes mistaken for gold may be mentioned pyrite and marcasite, and especially chalcopyrite. Grains of the latter, in polished faces of ore, often closely resemble gold in color and luster. Thin flakes of biotite and other micas, especially when partly oxidized, and other micaceous minerals, such as hematite and limonite, may also imitate it closely.

In panning or concentrating, many people have been misled by heavy lead minerals of a yellow color, such as the molybdate, chromate, tungstate, and even the phosphate, but these are distinguishable under a lens or low-power microscope by their brittleness and transparency. Some of the numerous basic sulphates of iron are at times difficult to distinguish from gold when exposed on freshly fractured vein stuff. Particles of natural or artificial litharge, brass, or "spelter solder," and even superficially oxidized lead alloys, sometimes bear an astonishing resemblance to gold. These, and specks of native copper or copper from blasting caps, may find their way into mine samples or drillings and be found in panning.

[1] A revision by the editor, in 1944, of the chapter contributed to the first edition by W. J. Sharwood.

On the other hand, mustard gold, resulting from oxidation of telluride, may have a distinctly earthy luster, and gold of low fineness may be easily overlooked.

Native silver and the chloride characterize the oxidized zone of most deposits. Native silver, usually nearly pure, occurs in very fine particles, threads, etc., and sometimes in masses which may reach several thousand pounds weight. In the Michigan copper mines, pure silver and pure copper occur attached and intergrown. Some native silver contains a little mercury. Coarse lumps are best hand picked, but the smaller are concentrated, or amalgamated, and the fines cyanided.

The chloride ($AgCl$) is readily reduced to metal by contact with metallic Fe, Zn, Al, or even Cu in contact with an electrolyte, and is then easily amalgamated by mercury. Alkaline cyanide, or thiosulphate solution, dissolves it readily, and also silver bromide and iodide, which often accompany it; strong solutions of chlorides have less solvent action.

The sulphide (Ag_2S) dissolves in strong cyanide solution, but not in chlorides or thiosulphates. It is slowly amalgamated by mercury when in contact with an electrolyte, and the action is facilitated by thiosulphates and copper salts, especially in the presence of metallic iron, etc. When roasted it yields Ag_2SO_4, which is somewhat soluble in water.

The numerous complex sulphur-arsenic and sulphur-antimony compounds of silver are not so readily amalgamated unless roasted; they are decomposed by grinding with metallic aluminum and sodium hydroxide or carbonate.

Galena often contains silver in the form of sulphide; and the selenide (Ag_2Se) and occasionally the telluride (Ag_2Te) occur in small amounts in some gold and silver ores, and apparently in some copper deposits.

Gold and Silver Alloys.—Pure gold is distinctly softer than silver; either is hardened by the addition of a small proportion of the other, or of copper or other base metal. In gold-silver alloys the maximum hardness occurs with about one-third silver. Small additions of silver reduce the gold color materially, but affect the melting point very little up to about one-third silver. Electrum is gold, especially the native metal, containing 15 to 45 per cent silver, rendering it pale. Green gold is a similar alloy containing about 10 per cent silver. The red-gold alloys contain copper.

Jewelers' gold usually ranges from 18 (Au 750) to 10 k. (Au 416) and frequently contains both copper and silver as alloy. The lower grades often contain some zinc, which helps to counteract the redness due to copper. They are sometimes made by alloying brass with gold, but extreme care is necessary to avoid certain impurities in the brass or copper used, especially lead or arsenic, which cause brittleness. British gold coin is 22 k. (Au 916.6), but alloys as low as 9 k. (Au 375) are recognized and hallmarked in England.

The proportions of copper and silver are determined by the color of the gold desired. Thus in 18-carat gold, 10½ per cent Ag and 14½ per cent Cu gives a dark tone; while 14½ per cent Ag and 10½ per cent Cu gives a light tone to the alloy. The compositions in the tables on page 291 are approximately correct.

White gold is properly an alloy of gold with palladium; if legitimately stamped 18 k., it will contain 18 parts gold (Au 750) and the remaining 6 parts are palladium, with usually a little silver. This alloy has a pure-white color and a high melting point. Palau and rhotanium are similar. A cheap imitation is produced by melting gold with a nickel alloy. The mixture sold for producing "white gold" by adding it to fine gold is Cu, 55 per cent; Zn, 21 per cent; and Ni, 24 per cent. A similar mixture for producing "green gold" is merely brass: Cu, 67 per cent, and Zn, 33 per cent.

For soldering gold there are many recipes, the aim being to produce an alloy considerably more fusible than that of which the object is made, but not differing much in color. Many of these soldering alloys contain a considerable proportion of zinc

with copper, silver, and gold; with copper, a considerable percentage of zinc does not cause brittleness, though the alloys are often extremely hard and difficult to roll. In recent formulas, cadmium is substituted for zinc. Such solders lose zinc (or cadmium) by volatilization when heated, becoming gradually less fusible.

Carat	Fineness	Per cent Au	Ag	Cu	
24	1000	100			
22	916	91.66	4.16	4.16	English standard
..	900	90	5	5	Metric standard
20	833	83.3	8.3	8.3	
18	750	75	10.4	14.6	Dark
18	750	75	14.6	10 4	Light
14	583	58.3	25.0	16.6	
14	583	58.33	4.16	37.5	
10	416	41 6	16.6	41.6	
..	....	62.5	22.5	13.0	Solder
..	. ..	54.5	31.75	13.75	Solder

The silver alloys are used for coinage, plate, solders, etc.

	Per cent Ag	Cu	Zn	
Sterling silver.	92.5	7.5		
Rupee silver...	91 6	8.3		
Standard silver... ...	90.0	10.0		
Solder:				
Hard..........	80.0	13.2	6.8	
Medium.....	75	20	5.0	
Pure silver..... ...	72	28	.....	Melting point 778°C.
Plate........ . ..	64.5	22.5	13.0	
Chain....	62 5	31.25	6.25	
Quick....	57	27.5	11.5	Sn 4 per cent. For resoldering
Bureau of Standards.	40	14	6	Sn 40 per cent. Melting point 400°C.

Aluminum forms a number of alloys with gold; one of these ($AuAl_2$, 22 per cent Al) has a remarkable purple color. The so-called aluminum gold is an alloy of copper with about 25 per cent Al, very slightly attacked by nitric acid, and closely resembling gold in color, but of low specific gravity.

Pure silver when melted absorbs oxygen from the air (up to twenty-two times it own volume) unless air is displaced by some other gas or the fused metal covered with borax, salt, or charcoal. On cooling to near solidification this oxygen is given off suddenly, the surface of metal sprouting or spitting. Small proportions of foreign metals usually prevent this. The oxygen is probably retained by fused metal as a suboxide, like that held by copper after solidification. Gold does not absorb oxygen.

When gold or silver containing a small percentage of lead is heated, or is kept just below solidifying point, a eutectic rich in lead exudes or liquates out; this often oxidizes, producing a peculiar "vegetation" on the surface. This is due to formation

of PbO mixed with minute globules of gold (or silver). In extreme cases the entire alloy may form a soft cauliflower-like mass.

The small proportion of silver alloyed with native gold and mill bullion is of some economic importance, usually more than covering cost of marketing refined bars. Assuming silver at 50 cents per oz., the per cent of gross value due to silver is as follows:

Ratio		Percentage, silver value
Gold	Silver	
900	100	0.16
800	200	0.32
700	300	0.60
600	400	0.95
500	500	1.43

With silver at $1 per oz., these figures would be nearly doubled, and for other values nearly proportional.

A minute proportion of lead—less than 1 part in 1000—makes gold brittle, especially when hot. This seems to be due to a highly fusible eutectic, which can be seen between the crystals of pure metal in a polished and etched section. Similar effects are produced by Bi, Te, Sn, Sb, As; while Zn and Cd in fair proportions yield less brittle alloys. Annealing removes brittleness due to traces of Pb, not that due to Bi or Te. Silver is similarly affected by most of these elements.

Tellurium renders gold extremely fusible; on heating in air the tellurium is slowly volatilized or oxidized, leaving bright globules of gold still retaining some tellurium.

Gold combines or alloys readily with tellurium, and with fusible metals generally, forming fusible alloys; it is not attacked by the vapor of selenium or sulphur. Silver is at once attacked when heated in the vapor of S, Se, or Te, forming Ag_2S, Ag_2Se, or Ag_2Te; like gold it alloys readily with fusible metals.

Gold resists all single acids, but is readily attacked by aqua regia; the most effective proportions are 1 part nitric to about 4 parts strong hydrochloric acid; any mixture of hydrochloric acid with a nitrate, nitric acid with a soluble chloride, or sulphuric acid with a nitrate and a chloride similarly attack it. It is very slowly acted upon by hot solution of ferric chloride. Moist chlorine gas converts gold into $AuCl_3$. Silver combines superficially with Cl, the AgCl then protecting the metal unless removed by some solvent. For this reason Au-Ag alloys are not dissolved completely by aqua regia unless the AgCl is removed from time to time from the surface by scouring or by some solvent, such as ammonia, cyanide, or hyposulphite.

Gold-chloride solutions ($AuCl_3$, $HAuCl_4$, $NaAuCl_4$, and other chloraurates) are reduced to metal if evaporated and gently heated, and are also reduced to metal by nearly all reducing agents such as base metals generally, SO_2 and salts of Fe'' and Sn''. Silver is readily dissolved by nitric or hot sulphuric acid, NO or SO_2 being evolved, but resists most others. Silver nitrate, sulphate, and chloride are not readily decomposed but may be heated without decomposition; they are easily reduced to metal by contact with base metals, Zn, Fe, Cu, etc.

Parting.—The cupellation of lead removes it as oxide, together with other base metals, leaving gold and silver. Silver-bearing lead may be enriched by the Pattinson process, in which crystals of pure lead are removed, leaving the more fusible eutectic, the process being carried on in stages and the enriched lead finally cupeled Silver

and gold may be more readily removed from lead by the Parkes process, in which a small percentage of zinc is added which, on cooling, crystallizes and rises (zinc being insoluble in solid lead), carrying up the precious metals as a crust, which is removed and refined.[1]

Gold and silver are separated or parted by means of nitric acid, NO being given off and $AgNO_3$ formed. This requires the ratio Ag:Au to be at least 2:1, though 3:1 was formerly preferred. Hot sulphuric acid also dissolves silver away from gold if the proportion of silver is large enough, SO_2 being evolved. Gold containing relatively little silver must have silver (or in some cases base metal may be used) added to reduce the gold to such a proportion that it will not protect the silver from attack.

It is preferable to use the Wohlwill process, electrolyzing the gold in a solution of $HAuCl_4 + HCl$, with gold cathodes, an alternating current being sometimes superposed upon the high-density direct current used. Silver remains insoluble as AgCl.

Silver containing but little gold is electrolyzed in a slightly acid solution of silver nitrate, with a silver or carbon cathode, leaving gold insoluble; this is used in the Moebius and Balbach-Thum processes.

The following tabulated data are of value in connection with the refining of gold and silver:

	Gold	Silver	Copper
Melting point, degrees centigrade	1063	961	1083
Specific gravity	19.3	10.5	8.95
Specific volume (cubic centimeters per gram)	0.0518	0.0952	0.1117
Cubic inches for 1,000 troy oz. = 1,898/sp. gr.	98 3	180.8	212
Cubic inches for 100 lb. avoir. = 2,770/sp. gr.	143.5	263.8	309.5

In an alloy containing G per cent gold, C per cent Cu, and S per cent Ag, the specific gravity is very closely

$$\frac{100}{0.0518G + 0.0952S + 0.1117C}$$

Cementation is an ancient method of freeing gold from silver and base metals. The metal was first granulated by pouring into water, or beaten into thin plates. It was then placed in crucibles with a large proportion of aluminous earth and heated; silver, etc., was slowly oxidized (or possibly converted into sulphate or sulphide) and absorbed. Most recipes, however, include common salt and burned clay or powdered brick, tile, etc. When heated in contact with these, silver chloride is formed, fused, and absorbed. Gold treated several times in this way ("seven times tried in the fire") was rendered nearly pure.

Sulphur or pyrite was also used; heated in sulphur vapor, most of the silver and copper form Ag_2S and Cu_2S, which can be mechanically removed.

In *Guss and Fluss* parting, an alloy, containing at least 50 per cent gold, was heated in a crucible with 3 parts antimony sulphide, and poured into a mold; the gold, alloyed with antimony, etc., is found at the bottom and easily separated from the layer of "plachmal" above it. This gold alloy was then fused with 2 parts antimony sulphide, and the product again with 1 part. The process was repeated if necessary until

[1] See pp. 201 to 208.

enough silver had been removed, when the gold was finally melted with borax and the alloyed antimony oxidized by a blast of air.

In the sulphur-litharge process (*Pfannenschmied*) a granulated alloy, rich in silver, was heated with sulphur, yielding Ag_2S, in which gold is disseminated. To collect the gold, a small percentage of litharge was added, yielding a fusible lead-silver alloy, which carried down most of the gold; a second or third treatment removed practically all the gold. Metallic iron was sometimes used instead of litharge to reduce a portion of the silver and collect the gold. Reduction of the remaining sulphide yielded a fairly pure silver.

Gold bullion, rendered brittle by Te, Bi, Pb, etc., may be softened by throwing a little $HgCl_2$ on the fused metal, also by adding solid AgCl or Ag_2SO_4, by stirring with Cl gas or an air blast; stirring with $NaHSO_4$, $NaNO_3$, or MnO_2 is also effective. More or less silver may be removed by these methods, especially by Cl $NaHSO_4$.

Recovery of Gold and Silver.—All gold and silver ores yield a high percentage of their precious metal when smelted with lead or copper ores, and an almost complete saving of them is effected in refining the lead and copper recovered. A large proportion of the silver of the world, and a considerable amount of the gold, is thus obtained as a virtual by-product from the smelting and refining of lead and copper ores, including some zinc-lead and zinc-copper ore. Some of this precious metal comes from concentrate, some from siliceous ore used as flux; comparatively little true gold or silver ore is directly sold for smelting. Smelting charges and deductions on the full weight of ore, with the cost of freight and loading, often make it advisable to adopt some method that may be far inferior metallurgically, as regards percentage recovery, but that puts the precious metal in a form in which it is more readily salable, such as bullion or rich precipitate.

Outside of smelting and refining, the present-day metallurgy of gold and silver may be summarized under three heads: mechanical methods (concentration, flotation, and blanketing, etc.), amalgamation, and the cyanide process. Chlorination of gold and hyposulphite leaching of silver ores were practically superseded by cyaniding by the year 1900; chloride volatilization and other promising processes have not yet assumed commercial importance. The products of concentration and flotation may be either smelted with lead or copper ore, or may themselves be treated by amalgamation or cyanidation. Each of the latter processes consists of five essential steps.

Amalgamation:
- Comminution of ore.
- Bringing ore in contact with mercury (and with chemicals in the case of silver minerals).
- Separating amalgam.
- Retorting amalgam to remove and recover mercury.
- Melting and refining the crude bullion from the retort.

Cyanidation:
- Comminution of ore (often combined with auxiliary processes of amalgamation, concentration, or classification, neutralization, or washing out soluble salts).
- Dissolving gold and silver.
- Separation of solution from ore, and washing residue.
- Precipitating gold and silver from solution.
- Refining precipitate and melting bullion.

The treatment of placer deposits is a special case of concentration, often combined with amalgamation.

PERCENTAGES PRODUCED BY DIFFERENT PROCESSES IN THE UNITED STATES
(*Mineral Resources, U. S. Bureau of Mines Yearbook,* 1940.)

	Gold					Silver				
	1936	1937	1938	1939	1940	1936	1937	1938	1939	1940
Placers, mainly dredging......	23.9	24.6	27.9	28.6	31.0	0.2	0.2	0.2	0.3	0.3
Amalgamation...........	27.1	25.3	23.1	21.1	19.7	0.7	0.5	0.4	0.4	0.3
Cyanidation................	18.8	19.3	22.6	22.3	21.4	4.1	4.3	7.0	7.1	7.5
Smelting ore and concentrate...	30.2	30.8	26.4	28.6	27.9	95.0	95.0	92.4	92.2	91.9

In South Africa about 65 per cent of the recovery is by amalgamation, 35 per cent by cyanidation; on the Mysore Field, India, nearly 90 per cent by amalgamation.

PERCENTAGES BY WEIGHT FROM VARIOUS SOURCES IN THE UNITED STATES

	Placers	Dry or siliceous ores	Copper ores	Lead ores	Zinc ores	Copper-lead and copper-zinc ore	Lead-zinc ores	Total ounces
Gold.								
1906...	28.24	63.17	5.77	1.29	0.02	1.26	0.25	4,703,000
1907....	28.22	62.11	6.44	2.56	0.14	0.05	0.48	4,227,500
1914....	25.30	66.56	6.00	1.69	0.04	0.01	0.40	4,418,000
1915....	22.66	67.57	7.22	1.78	0.10	0.05	0.62	4,754,500
1920....	25.3	63.93	7.18	1.96	0.15	0.16	1.32	2,383,000
1921....	28.89	66.02	2.25	2.64	0.003	0.007	0.19	2,345,000
1940....	31.0	55.5	11.2	0.36	0.003	2.00		4,869,949
Silver:								
1906....	0.30	29.27	27.69	26.72	0.17	11.88	3.97	57,362,450
1907....	0.24	36.27	26.58	32.99	0.18	0.93	2.81	52,497,060
1914....	0.22	39.95	21.30	27.72	0.21	0.36	10.24	69,623,200
1915...	0.21	35.53	25.96	27.40	1.57	0.33	9.00	72,353,700
1920....	0.13	36.22	21.49	30.19	2.23	1.18	8.56	56,536,900
1921....	0.18	51.88	10.36	32.30	0.01	0.97	4.30	46,171,300
1940....	0.28	40.5	29.0	4.4	0.03	24.2		70,549,362

The commercial ratio between the values per ounce of gold and silver was about 15 to 16 from 1800 to 1873; since 1873, the annual average has ranged from 18 to nearly 40. One of the largest producers turns out about a ton of silver per day; one of the largest gold mines has for years yielded a ton of fine gold per month; the value of the silver is much less than that of the gold.

To generalize roughly, a gold deposit, under extremely favorable conditions, may be profitably dredged when containing only 1 part in 10 millions, or 11 cents per ton; 1 part in a million assures a reasonable profit in a placer. A gold ore containing 10 parts per million ($11 per ton), while of low grade, is assuredly profitable if not too small or unfavorably situated; and half or even one-third of this value may be payable if very large and otherwise advantageously situated. Silver ores begin to be of commercial importance when containing about 100 parts per million, or 3 oz. per ton.

When associated with commercial ores of copper and lead, they are extractable at negligible cost and in such cases smelters usually pay for over 0.025 oz. Au or 1 oz. Ag.

World Production of Gold and Silver, 1939

Reported by U.S. Bureau of Mines and Director of the Mint

Source	Gold, oz.	Silver, oz.
United States	5,559,139	57,808,000
Canada and Newfoundland	5,114,692	24,584,689
Mexico and Central America	1,017,623	80,668,824
North America	11,691,454	163,061,513
South America	1,775,661	31,551,087
Europe	5,644,143	21,861,870
Asia	2,657,687	22,386,996
Africa	15,510,377	4,618,209
Oceania	2,210,346	14,621,894
Total	39,489,668	258,101,269
Total United States production 1792–1940	262,487,295	3,650,909,393

Gold in Sea Water.—Gold and silver have long been known to exist in the waters of the ocean, and occasional projects are brought forward to recover the gold. The statement of Sonstadt that the gold in sea water is "less than 1 grain per ton" is often interpreted as meaning at least 1 gr. The actual average is probably less than $\frac{1}{40}$ grain or $\frac{1}{10}$ cent per ton, and entirely below the present economic limit for extraction. Even at this low estimate, the aggregate amount in the ocean (estimating the ocean at about 320,000,000 cu. miles, each of 4,600,000,000 tons of water) is enormous.

Metallurgical Systems

Most of the modern metallurgical schemes for gold and silver ores are covered by the following outline:

1. Preliminary breaking by crushers of jaw or gyratory type.
2. Crushing:

Dry:

By rolls or disks (with or without screens to return oversize).

Wet:

Stamps alone.

Stamps followed by . . . pebble mills.

Ball mills or rod mills followed by . . . pebble mills.

Heavy stamps with coarse screens, chileans, ball mills, or rod mills . . . pebble mills.

The rotary mills are generally run in closed circuit with classifiers.

Dry crushing:

Followed by cyaniding (with or without preliminary water or alkaline wash)

Wet crushing:

In water (with or without amalgamation or concentration) — Draining or dewatering — Cyaniding.

In cyanide solution with or without amalgamation or concentration.

With special reagents followed by cyaniding (such reagents as H_2SO_4, SO_2, or aeration in presence of lime).

3. Treatment of crushed product:
   - Straight cyanidation (with or without prior amalgamation), and either without roasting or after roasting to destroy carbonaceous matter or sulphur compounds.
   - Concentration (with or without amalgamation) by tables, vanners, corduroy blankets, canvas, or flotation.
     - Concentrate:
       - Smelted, or sold to smelter.
       - Cyanided (intensively), raw or after roasting.
       - Amalgamated, then cyanided.
     - Tailing:
       - Discarded, if crushed in water and low grade.
       - Cyanided.
   - In case of cyanidation of original product or of tailing there is:
   - Classification into sand and slime (with or without partial regrinding).
     - Sand:
       - Leached with cyanide solution.
     - Slime:
       - Discarded, if crushed in water and low grade.
       - Cyanided, by agitation or in filter press.
   - All-sliming:
     - Cyanided, by agitation or in filter press.
4. Separation of cyanide solution from ore or tailing:
   - Filtration:
     - Gravity (sometimes aided by vacuum) for coarser leached products.
     - Vacuum or pressure (in basket filters for fine products, intermittent).
     - Vacuum with rotary filters (continuous) sometimes in series.
     - Pressure in filter presses (intermittent).
   - Decantation:
     - Intermittent, after settling.
     - Continuous, with intermittent or continuous final filtration.
     - Continuous countercurrent, with thickeners in series, with or without final filtration.
5. Precipitation of gold and silver from cyanide solution (preferably deaerated by vacuum treatment, and clarified if necessary):
   - Zinc shaving in boxes with compartments for upward flow.
   - Zinc dust in filter presses.
   - Aluminum dust in filter presses.
6. Refining precipitate:
   - Preliminary acid treatment for removal of zinc, etc. (often omitted), or calcination.
     - Direct fusion with fluxes in crucibles or on hearth.
     - Lead refining: briquetting or mixing with a litharge-borax flux, fusing on reverberatory hearth or in blast furnace, followed by cupellation of rich-lead bullion. Treatment of by-products usually necessary.

Generally, removal of free gold at an early stage of treatment tends to minimize the dissolved gold discharged with residue or tailing. On the other hand, in "all-sliming" the cyanide process is simplified by omitting amalgamation. If coarse gold is not amalgamated, it must be removed by mechanical methods or ground sufficiently fine to ensure rapid dissolution. Some Canadian plants are giving a bulk flotation to the cyanide tailings in a circuit rendered somewhat acid with SO_2. The

concentrate is roasted to produce further SO_2, and then cyanided. The process is said to yield a profit on a 30 cent tailing.[1]

MECHANICAL TREATMENT[2]

Mechanical Separation

Alluvial Concentration.—In handling alluvial material the main problem is to get rid, at the first opportunity, of most of the boulders and coarse gravel, without losing any of the gold originally adhering to them, and to disintegrate rapidly and completely any lumps of sticky clay that would carry fine gold further down the sluices or even into the tailing. It is not generally desirable to crush any of the pebbles.

In hydraulic work the coarse gravel running down the sluices does much of the work of disintegration, and the coarser portion is removed when desired by means of "undercurrents" or grizzlies of steep grade, which allow the finer material to pass through and conduct it to boxes or tables where conditions are more favorable for settling. After passing over the grizzly, the coarse gravel may be discarded or returned to the main stream.

A revolving trommel with lifters, and furnished with ample water sprays, is an ideal device for performing these operations on a large scale, and is now standard practice for dredges, the pebbles acting as disintegrators. By graduating the diameters of the holes to suit the material handled, a comparatively uniform discharge may be obtained throughout the length of a trommel, but by far the largest part of the gold passes the holes near the inlet end. Shaking screens have been used but consume too much power. One of the older "cement mills" for hard gravel was virtually a large trommel built of railroad or T iron. Another cement gravel mill is a pan with a stout vertical shaft carrying agitating arms, and fed with water, accumulated coarse rock being discharged at intervals by opening a door in the side or bottom.

In small operations, the same results are achieved by using a rocker with punched screen, fed a few pounds at a time; or by shoveling into a sluice box, at the head of which is a screen or set of bars, over which the material may be manipulated by a sluice fork or shovel.

The length of wooden sluice boxes is standardized at 12 ft., and a grade of 6 in. means 6 in. per box, or about 4 per cent, the width varying with the load. For small, semiportable boxes, the upper end of the bottom is sawed 2 or 3 in. wider than the lower end, so that they fit closely one in the other.

In large hydraulic work, boulders of several tons weight may enter the sluices and must either be carried through or blasted or lifted out; such sluices require stout linings of wood or steel.

Various types of riffle material have been used: cross-grain pine blocks, roughly squared, or flat-lying blocks up to 4 × 6 in., either form being separated by small strips of wood or bits of rock; boulders or roughly squared rocks; peeled pine poles; planks mortised or bored, or iron blocks cast with channels or pockets, and railroad steel.

Hungarian riffles are strips of wood from about 1 to 1.5 in. square up to 2 × 4 in. laid crosswise with about equal spacing; they are often undercut on the downstream side, and have tops sloping upward. When subject to heavy wear, they are covered with strips of iron or steel, manganese steel being most durable. By attaching them to longitudinal strips they form frames readily removed. A similar riffle for dredges is built of 1¼- or 1½-in. angle steel riveted to 6-ft. strips of the same material; the

[1] *Mining Met.*, February, 1941, p. 72.

[2] Also see Concentration, p. 134, in the first volume, entitled "Principles and Processes."

angles are opened about 10 or 15 deg. above a right angle and point downstream. Another effective sluice lining is coconut matting covered with expanded metal (steel lath).

A special study of riffles for heavy work was made by P. Bouery at La Grange, who successfully used 40-lb. steel rails on 5-in. centers, resting on 2 × 6 in. pine strips set edgewise with spacers. He recommends invariably placing riffles crosswise A riffle of manganese steel designed by Bouery for severe hydraulic work consists of riffle proper, spacers, and lockers; when worn, these can be used as liners.

FIG. 1.—Hungarian riffles.

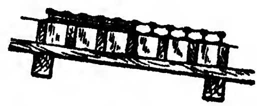


FIG. 2.—Bouery steel-rail riffle at La Grange.

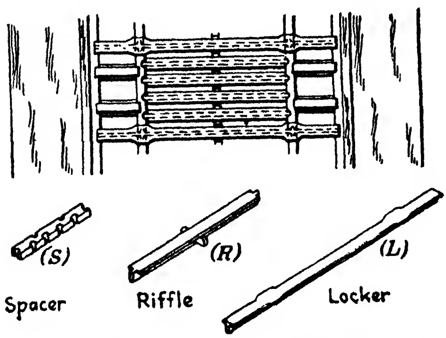


FIG. 3.—Bouery patent manganese steel riffle.

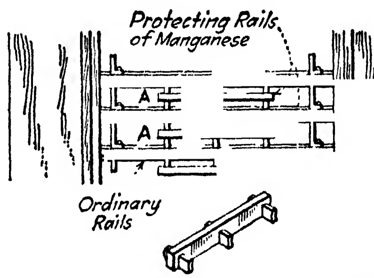


FIG. 4.—Railroad rail riffle with manganese protecting rails, at La Grange.

In cleaning up a sluice, clear water is run for some time; then, beginning at the head, the riffles are removed section by section, the dirt washed off, and the deposited gold washed down to the next section, where it can be scooped up into buckets. It is then taken to a point where it can be panned or treated in a rocker or special sluice to concentrate the gold further, and separate it from the accompanying black sand.

DISTRIBUTION OF GOLD IN SELECTED SLUICES AT LA GRANGE (*P. Bouery*)
(Boxes 1 to 4 were filled with pebbles, etc.)

Box number	Ounces of gold						Total ounces per 12-ft. box
	+10 mesh	+50 mesh	+100 mesh	+150 mesh	+200 mesh	−200 mesh	
5	45.8	50.7	1.38	0.36	0.31	1.45	100
6–16	18.0	83.3	2.33	1.00	0.31	0.83	43–108
22	1.73	20.22	3.08	0.70	0.25	0.62	26.2
48	0.18	2.18	1.06	0.12	0.05	0.16	4.15
88	0.018	0.12	0.47	0.008	0.026	0.005	0.65
136	0	0.053	0.027	0.043	0.011	0.01	0.14

Dredges.—The dredges now in general use have close-connected buckets of 5 to 15 cu. ft. capacity and are built of steel or wood, digging to a depth of over 80 ft. below the surface of the pond or stream in which they float.

The buckets discharge into a long revolving screen or trommel running at a grade of 5 to 10 per cent toward the stern, where the coarse material passes to the stacker, while the finer portion goes to the gold-saving sluices and may then be run out directly or may go to a second stacker. The land is usually left in a valueless condition, but resoiling is possible by the use of multiple stackers.

The screen may be cylindrical or stepped in diameter; it should have a baffle at the end of each section and must be well braced. In a large dredge it may be 10 ft. in diameter by 50 ft. or more, with a peripheral speed of 150 ft. per min. The perforations should be adapted to the material handled; one example has openings $\frac{3}{8}$ in. at the upper end increasing to $\frac{3}{4}$ in. at the discharge, another $\frac{1}{4}$ in. increasing to $1\frac{1}{4}$ in. The stacker belt may be up to 4 ft. wide, of eight-ply rubber, and will normally last a year or more. An internal spray pipe runs the full length of the screen, and two or more smaller ones outside; these must have an ample supply of water to wash the gravel and carry the fines over the sluices.

The sluices may be in one series or in two decks 4 or 5 ft. apart. They are usually about 30 in. wide, running crosswise of the deck at a slope of $1\frac{1}{4}$ to $1\frac{1}{2}$ in. per ft. (10 or 12 per cent) and then turning aft. Much the largest portion of the gold is caught in the first few feet of sluices; Janin mentions a 6-ft. dredge with 1457 sq. ft. of sluice area, catching 89 per cent of the total recovery in 292 sq. ft., or one-fifth of the total area. For more clayey material the area was increased to 3900 sq. ft. One 15-ft. dredge had 8000 sq. ft. of sluices in two decks; in another case 4500 sq. ft. in two decks was found needlessly large for a 15-ft. dredge digging 600 cu. yd. per hr. The head tables are usually kept covered with heavy screen to prevent theft.

A considerable saving is made on the save-all, a small sluice catching the drip from the descending buckets and discharging through the hull, and in the nugget catcher—a short, steep series of riffles over which the fines from the extreme end of the screen pass.

In some cases, as on the Yukon, no mercury is used, and the first section of each sluice is covered with coconut matting and expanded metal. The matting is taken up daily, folded, and washed, and the washings are passed over a special set of riffles. The product is cleaned by panning and finally by dry blowing, while the tailing goes back to the main riffle system. The riffles in the lower sections of the sluices are cleaned up at intervals of a week or two.

In California, mercury is more generally used, up to 3000 lb. weekly on the larger dredges and up to 1000 on the smaller. The loss of mercury in a 6-month campaign may range between 1 and 5 per cent of the total used. When cleaning up at intervals of a week or two, the riffles are lifted out, section by section, and washed off with a hose, and the dirt concentrated by temporary stops placed in the sluices. The concentrate thus obtained is shoveled out and washed in a small sluice box, the product screened, and the fines run through an amalgam barrel with a little additional mercury.

Sometimes a trough is inserted below a stop to divert the material being washed down into a clean-up box, about 2 × 3 × 1 ft. deep, having several centerboard mercury riffles, the tailing from which passes through a sluice with expanded metal riffles and back to the main dredge sluices.

In many localities, considerable quantities of lead shot, nails, and miscellaneous metallic scrap may be separated in screening the product, and this material may retain more or less amalgam and necessitate working over.

The "black sand" obtained as a by-product in cleaning up placer sluices often contains platinum metals in small proportions, as well as some gold; much of the gold

and platinum may be recovered by treatment with a suitable concentrator. The Senn machine has been found well adapted for this purpose.

Dry Concentration.—A clean-up of placer material is often finished dry. After removing the coarsest portion with a sieve, the remainder is "tossed" or jigged dry in a pan or shovel, using a circular motion; the sand thus brought to the surface is then blown off. The tailing thus obtained often contains fine or flaky gold.

Dry washers or concentrators are used under desert conditions. The success of all these devices depends on the material being perfectly disintegrated and thoroughly dry; clay, especially, must be pulverized. Several different principles have been applied:

1. Winnowing, by letting material fall vertically through a horizontal blast of air, which is either constant or rapidly pulsating. The wind is often utilized, and the gold caught on a sheet of canvas, but some efficient machines, as that of Edison, have been devised on this principle.

2. Passing the material over an inclined table covered with cloth, supported by wire screen through which a pulsating blast of air rises; the table may be fixed or oscillating, and is provided with low riffles.

3. Passing material over a reciprocating table of the Wilfley type, having a tight cover near the surface, a blast or numerous parallel blasts of air passing parallel to the surface under the cover.

4. Sized material is allowed to fall on a horizontal rapidly rotating disk (as in the Pape-Henneberg system), the particles being thrown to distances varying with their specific gravity.

Black Sand.—The treatment of the black sand or concentrate obtained from beach or alluvial deposits is usually crude and unsatisfactory. This material actually varies much in color; it often consists largely of magnetite and ilmenite, with other heavy minerals such as garnet, tinstone, columbite, or tantalite, and occasionally metals of the platinum group. The gold is retained by, but rarely contained in, the sand particles. The black sand separated by "blowing" at the final stages of a clean-up may show gold values up to $1 per pound.

Magnetic concentration is rarely of use, as much of the fine precious metal may be picked up mechanically with the magnetic concentrate, while in some cases some of the valuable materials are strongly magnetic. In some river gravels, and such beach sands as the Nome deposit, preliminary separation by 30- or 40-mesh, or finer, screens allows all the gold to pass and retains only pebbles of extremely low grade.

There is no apparent reason why black sand thus concentrated, or recovered from sluices, etc., should not be successfully treated by cyanide solution, after removing coarse gold by riffles or amalgamation. Early experiments are said to have failed in precipitation by zinc, but laboratory tests show no cause for difficulty.

Blanket Concentration.—Woolen blankets have long been used for catching gold at Brazilian mines, where mercury is sickened by bismuth and tellurium minerals, and they were introduced into early Californian and Australian mills and have been used in mills treating the richer Cripple Creek ore. They are generally laid overlapping on inclined tables, the pulp flowing over them for an hour or several hours, when they are folded, replaced by fresh blankets, and the accumulation washed off in a tank.

In 1918, corduroy was used to replace copper plates in the Van Ryn (Rand) stamp mill after adoption of coarse crushing (but not in the tube-mill section); the concentrate (0.27 lb. per ton milled, containing 2.1 per cent gold) was ground in a barrel with mercury, then passing to a mechanical batea. The loss of mercury in the barrel was only 0.01 oz. per ton milled.

In 1923, F. Wartenweiler announced the total elimination of plate amalgamation in two Rand mills, Modderfontein East using five overlapping rows of corduroy strips, which caught, respectively, 80, 11, 4, 3, and 2 per cent of the total catch. The area of corduroy was 1.26 sq. ft. per ton milled daily, and this might have been reduced nearly 50 per cent without serious detriment. The product (1.8 lb. per ton milled) was saved by hand washing, but washing machines might be used; it was treated on a Wilfley, and this concentrate amalgamated in a barrel, yielding 94 per cent of its gold content, 98 per cent of which was free. Corduroy and wool blankets were found equally effective, but corduroy gives a less bulky concentrate, and the lock-up of gold is very small. Canvas gave a still smaller bulk, but caught only 75 per cent as much gold; riffles were only 57 per cent as effective.[1]

Canvas concentration, as practiced in California, is particularly adapted to catching extremely fine free gold, galena, and telluride which occur in unsized pulp, and was originally suggested by Brazilian practice. It has been successful in treating tailing that has passed vanners, etc., and still carries 50 cents to $1 per ton.[2]

Heavy canvas is laid on a carefully built wooden floor, usually in strips about 22 in. wide, occasionally up to 6 ft., with strips of pine about 1 × 3 in. between for walking on. They are usually 12 to 16 ft. long and inclined 1 to 1.5 in. per ft., but have been made much longer and inclined ½ or ¾ in. Dressed 1-in. lumber is used, free from knots, preferably tongue and grooved, laid on inclined joists, and most carefully leveled. Two launders supply pulp and clear water at the head; one across the foot carries off tailing, and another beyond it the concentrate. After the pulp has run about an hour, the feed hole is plugged on two sluices and the clear water turned on, washing the light sand from the canvas into the tailing launder. As soon as the concentrate in the first sluice is clean, a board or iron sheet is turned or slipped under the lower end of the canvas to convey the stream to the concentrate launder, and the concentrate is sluiced down by a small additional stream from a hose with flat nozzle, or is slightly swept down with a broom. Two sluices are thus idle during cleaning, one sluicing and the next washing. The concentrate passes to a series of settling tanks, the last being provided with baffles. The product is fine, with little sulphide, often over 90 per cent gangue, usually $30 to $100 gold per ton, but sometimes much richer. The use of burlap in the tailings launders of Utah Copper to catch some gold minerals has already been commented on—30,000 sq. ft. is used for 24,000 tons of tailing per day, and the burlap is burned monthly.

Important points are perfect adjustment of slope on substantial foundations, equal distribution of pulp and avoidance of overload and dry spots, ample water supply, ample time and space for settling concentrate. Old canvas needs less water than new, producing less but richer concentrate; it may be turned when one side is worn smooth, and is at its best when the original fuzz has just disappeared. If a plant is shut down, it is advisable to keep the canvas wet or remove it and roll it up.

AMALGAMATION

Amalgamation.—Pure gold foil, annealed by gentle heating, is instantly amalgamated if brought into contact with clean mercury at room temperature. If hammered repeatedly, or if previously heated to the point of fusion, it is less easily amalgamated; silver and silver-gold alloys are also less amalgamable; and it is necessary to rub or scour copper with sand, or to treat it with acid or a cyanide solution,

[1] The use of blankets, cloth, and riffles for gold and other minerals is described in Agricola's Book VIII; see especially pp 309, 317, 328, and 331 of Hoover's translation Practice at Grass Valley, Calif., is described by J. A. Phillips, "Mining and Metallurgy of Gold and Silver."

[2] See Storms, *Eng. Mining Jour.* Vol. 60, p. 29, 441, 466, July 13, Nov. 9 and 16, 1895; Preston, California Gold Mill Practices, *Bull.* 6, California State Mineralogist.

to ensure amalgamation of the surface. Even when amalgamated, the mercury does not penetrate copper appreciably; gold is much more readily penetrated, and silver slowly. Gold and silver, if covered with a film of grease, oxide of iron, or tellurium, or of a sulphide, no matter how thin, refuse to amalgamate until the film is abraded mechanically or removed by a suitable solvent.

Similarly, coatings of oil or oxide on mercury, and especially the conditions known as "flouring" and "sickening," effectually prevent amalgamation of gold. This result may often be obviated by the addition of a little sodium amalgam, or by electrolysis (making the mercury the cathode), but too large a proportion of sodium may result in amalgamating iron and any other base metals in contact with the mercury.

Flouring may be brought about by agitating mercury with water or ore pulp and a trace of oil, or by distilling it from a retort containing a little grease or paper; in extreme cases it forms a mass of microscopic globules, like flour or white grease, which refuse to coalesce. Sickening is a similar, often indistinguishable, condition, induced by chemical means, as when the globules are coated with a film of oxide, sulphide, or chloride of the mercury itself or of some base metal contained in it. It may be caused by agitating mercury with finely divided, partly oxidized sulphides, or by perchlorides of iron, mercury, copper, or other persalts of these metals plus NaCl. Any appreciable impurity in mercury is usually recognizable by the globules losing the spheroidal form and acquiring a tail.

The extraction of gold from ore by amalgamation was practiced to some extent in ancient times, but no details of the methods are known. In the Middle Ages, rich ore and concentrate were ground or rubbed with mercury in wooden bowls using iron-shod mullers rotated by crude machinery. Later, batches of ore were ground fine with mercury in the arrastra, using stone drags on a stone-paved bottom. In recent times the amalgamation of gold has been almost entirely associated with the development of the stamp mill.

Three variants may be noted: inside amalgamation proper, in which a copper plate is inserted in the front of the stamp mortar, and sometimes a second inside plate at the back, mercury being fed with the ore at intervals varying from 15 min. to 2 hr.; outside amalgamation, in which all the reliance is placed on amalgamated copper plates outside the mortar, on which mercury is sprinkled from time to time; and an intermediate system, in which the mercury is fed into the mortar but no inside plates are used.

Disregarding the crude nonrotating stamps of earlier periods, gold milling since 1850 has included the following:

1. The light (500- to 750-lb.) stamps of early Californian and Australian practice, used three to six in a battery. The mortars were of various patterns, often low iron troughs with built-up housings of wood or sheet iron. The screen was often punched sheet iron or copper.

2. Wide mortars, supposed advantageous for amalgamation, used with stamps of 700 to 850 lb., and of high form. These rarely crushed 2 tons per stamp day, often only 1.25 to 1.5 tons through a 40-mesh or finer wire screen, usually brass wire, or punched tin plate. A drop of 6 or 7 in., ninety to one hundred times per minute, was common.

3. The extremely wide mortar characteristic of Gilpin County, Colorado, with light (600- to 700-lb.) stamps of high drop (about 18 in.) and only 30 per minute, was supposed to have special virtue as an amalgamator.

4. The extremely narrow, high-form mortar, usually associated with Homestake practice (1876) and designed for rapid crushing. An 850-lb. stamp at 88 drops of 10 in. crushed over 4 tons daily through a diagonal iron or steel slot screen equivalent to 30 mesh. Its crushing efficiency has led to the wide use of this pattern and vari-

ations of it adapted for heavier stamps. The narrow form is not necessarily inimical to amalgamation, as it has not been uncommon to find over 50 per cent of the total recovery in the mortar, collected almost entirely on the narrow (5 or 6 in.) chuck-block plate.

5. The more recent heavy stamps, in American and especially in African practice, which have ranged from 1200- to 2000-lb. weight, about 1500 lb. being perhaps more generally preferred. These have tended constantly toward coarser crushing, with screens approaching ¾ in. in aperture, the product of over 10 tons per stamp passing to rod mills, ball mills, or pebble mills. With the heavy castings, long heads, etc., necessary for heavy weight, the open-front mortar has been revived; and the coarseness of crushing has encouraged the abandonment of inside amalgamation.

Five stamps per battery was early recognized as standard practice, mortars discharging in front only, and fed with Challenge feeders. Two-stamp mortars have been little used except for prospecting, but excellent results may be obtained with them and with some of the one-stamp mills, of which the Nissen is probably the best. This has been made of 2000-lb. falling weight, with a circular mortar half surrounded by screen. Some others have screen on three of the four sides.

Steel-wire screen is now much used, with either square or rectangular openings, often slotlike, with double wires in one direction and heavily crimped. In fine crushing, sheet steel is often used, punched with diagonal slots ½ in. long, or thin tinned iron plate with round punched holes. The modern screens are almost always set vertical.

In place of a long line-shaft drive, one electric motor now usually drives 10 light or 5 heavy stamps, by a built-up wood pulley 7 or 8 ft. in diameter with a 14- to 18-in. belt, the shaft running in plain cast-iron bearings without cover. Wrought-iron camshafts are preferable to any steel ordinarily obtainable. The cams are preferably attached by the Blanton self-locking device, which allows of easy removal, all the cams being interchangeable in position.

The standard cam curve is the involute of a circle, the center coincident with the camshaft axis and the radius the distance from the axis to the central plane of the stamp stems. The involute gives uniform speed of lift, but strikes the tappet with a sudden jar, and the curve is often much modified at root and tip. The gib tappet may have two or three keys. The usual order of drop is 1, 3, 5, 2, 4 (identical with 1, 4, 2, 5, 3), the only combination possible if no adjacent stamps drop consecutively, but 1, 5, 2, 4, 3 (= 1, 4, 2, 3, 5) is also used, and occasionally others in which one adjacent pair drop consecutively. Any tendency to bank sand at one end of mortar is usually overcome by giving the end stamp a slight increase in drop. Various forms of guide are used but generally have cast-iron liners in place of the wood formerly used.

For stamps from 800- to 1500-lb. weight the following table gives the range of weights commonly adopted. The last column shows the greater range of weight used for heavy stamps in South Africa and India. The percentages are based on falling weight with new shoes.

	800 to 1,500 lb., per cent	1,250 to 2,000 lb., per cent
Stem	42–44	47–28
Tappet	16–13	10–14
Boss	26–28	22–40
Shoe	17–14	20–13

The corresponding cam weight ranges from 25 per cent with light, to 20 per cent with heavy stamps, all being about 32 in. across tips. The camshaft ranges from (for 10) 30 per cent above the falling weight for light up to 50 per cent above for heavy stamps ($5\frac{3}{8}$ to $6\frac{15}{16}$ in. by 14 to 16 ft.); stems increasing from 3 in. at 800 lb. to 4 in. at 900, and usually 14 ft. long; shoe diameters 8.5 in. up to about 900 lb., and 9 in. above that.

Mortars are always of the high form, of heavy cast iron, generally with front entirely open, but variously proportioned. Reinforced concrete is now in general use for mortar supports, with an intermediate cushion of wood and rubber or belting. The ends and back of mortars are often protected by liners of chrome or manganese steel.

Battery water should be supplied at the rear of the mortar at two or more inlets; the ratio of water to ore stamped has varied widely, ranging from 2.5 in occasional Californian mills to 10 or 12 in former Homestake practice, high crushing duty and amalgamation being obtainable at both extremes—5 to 8 is generally preferable. With plate amalgamation, the water and grade must be sufficient, and the distribution of pulp over the topmost plate even enough to produce uniform waves and avoid building up islands of sand. For successful amalgamation the temperature of the feed water should be uniform, and neither extremely cold nor hot. Practically all the energy expended in crushing reappears in the increased temperature of the pulp, which is of importance in cold climates.

Amalgamation.—Mortars formerly had inside plates both front and back 6 or 8 in. wide and extending across the full length; the back plate has been discarded and the front plate—usually about 5 or 6 in. by 14 in. thick—is attached to the chuck block immediately beneath the screen; even this is now obsolescent and is seldom used with heavy stamps.

A "lip plate" is sometimes attached outside the mortar, extending across the discharge and 1 to 2 ft. wide. The main apron plate may be in one unit or more, each 4 to 5 ft. wide by 8 to 12 ft., of 18-in. soft-rolled copper. In successive units, the width should be maintained or increased. Long plates are usually set in an unbroken sheet of 8 to 24 ft., but some operators claim an advantage in cutting them into 2-ft. lengths, set with a drop of an inch or two at each step; the long plates are easier to clean and care for. Plates of Muntz metal have been used in New Zealand and elsewhere with apparent success; at several mills in the United States they have been a total failure. The plate table is best built of tongue-and-grooved lumber, 1.5 or 2 in. thick, with 2-in. sides, and may be made adjustable in slope. Planed cast iron has been used. The plates are secured by screws or copper nails, and cleats are often added at the sides. If divided longitudinally into two or three runs, it is easy to clean one run at a time without stopping the battery.

The inclination of plates is best kept from 1.5 to 2.5 in. per ft. (12.5 to 20 per cent) depending on the proportion of water, fineness of pulp, and proportion of heavy minerals, but extremes of $\frac{5}{8}$ in. up to 3 in. per ft. have been used. The plates are usually placed close to the mortar, but sometimes the pulp is transported some distance and then redistributed over a plate system. This sometimes results in large accumulations of amalgam in pipes or launders.

Silver plating of the copper plates is advantageous, except with rich ore, and in the case of the plate next the mortar; about 2 oz. silver per square foot is a suitable amount, or soft silver amalgam may be rubbed on the plate. In "setting" new copper plates, about $\frac{1}{4}$ oz. mercury per square foot is requisite, and this should be applied by scouring with wet sand and a little weak solution of sodium cyanide.

Various amalgam or quicksilver traps have been used, but there is probably nothing better than a shallow transverse trough or riffle about 2 in. deep and 4 or 5 in. wide

at the foot of the plate table. The accumulated concentrate from this may be collected daily with a small scoop and carried in buckets to a central point, where it can be run over a special plate or riffles, or ground in a pan or small ball mill.

Many mechanical amalgamators have been devised and used, such as horizontal rotating cylinders lined with copper, or provided with copper wings or lifters, or arrangements of horizontal disks or shelves rotating on a vertical axis, series of shelves of sheet copper, etc. The Pierce amalgamator is probably the only one of these to show greater efficiency than a plain plate. Numerous electrolytic devices have also been used, as well as sodium and zinc amalgam, to maintain the surface of mercury in a bright condition.

It is remarkable that gold or amalgam, while escaping all the contrivances arranged to catch it, often accumulates in unexpected places, such as angles of cones, sumps, and launders, the rakes of Dorr classifiers, and on the runners of high-speed centrifugal pumps. All such places should be inspected from time to time, and any tendency to build in launders should be encouraged by placing riffles suitably safeguarded.

Plate Area.—The relation of plate surface to stamps and stamp capacity varies remarkably in the practice of different fields. Some extreme cases may be noted:

Mine or district		Approximate percentage of product amalgamated	Square feet plate area	
			Per stamp	Per ton per day
Treadwell, Alaska—880 stamps, 1904		50	9	2
Homestake, S. D. Amicus mill, 240 stamps	1910	70	62.1	13.6
	1923 with tubes	66	43 3	7.8
Pocahontas mill, 160 stamps	1910	70	32.7	7.5
	1923	66	18.0	3.6
South mill, 120 stamps	1923 with rod mills	66	25.6	1.6
Rand, South Africa—Typical mill with tube mills		65	10	1 2
Ooregum, India—55 stamps, 1923 with tubes		88	20	2.2

With the revival of blanket practice the tendency is to reduce plate area still further.

Loss of Mercury.—In gold amalgamation, an ounce per ton was not an uncommon loss in early practice, and occasionally much higher losses were recorded, but this has been much reduced. At the Treadwell mines, shortly before abandoning amalgamation, the loss varied from 0.06 to 0.08 oz. per ton with ore from $1.50 to $2.50; at the Homestake, 0.06 oz. was lost with low-grade oxidized ore, and 0.17 oz. with $5-ore containing sulphides, and a similar range has prevailed in South Africa. At Modderfontein East, amalgamating corduroy concentrate, about 0.05 oz. is reported.

Among the principal sources of loss are drops running from the end of plates kept too "wet," and flouring.

Outside plates usually have the amalgam removed once every 24 or 48 hr. by washing off sand and then brushing thoroughly after sprinkling with some additional mercury. The amalgam may then be collected at one spot by means of a stiff brush or cloth, or a rubber scraper, and transferred to an iron kettle. Any hard crystalline accumulations should be carefully scraped off before they become persistent. With a

properly organized system the entire time consumed is about 1 min. per stamp per day.[40] In many mills the plates are also "dressed" or brushed up at intermediate periods, and may be sprinkled with mercury at the same time. Inside plates are usually removed for cleaning about twice a month, a clean plate being exchanged for the one taken out. The entire mortar is cleaned out about once a month, or whenever dies are taken out.

The actual absorption of precious metal into the body of a copper plate is negligible, but the accumulation on the surface may amount to many dollars per square foot if accretions of hard amalgam are allowed to build up, as they sometimes do, to a thickness of ⅛ in. or more, thus tying up an important amount of gold. In some mills this layer is softened by the occasional application of steam or hot sand, which facilitates its removal by scraping, but it is better to avoid this condition by daily removing hard accretions. Absorption only occurs when the rolled copper plate has capillary openings, such as minute cracks or pinholes.

Amalgam obtained from plates, etc., is cleaned by grinding with water and additional quicksilver, the floating impurities being wiped from the surface with a sponge, or in small lots by pouring from one vessel to another, when pyrite, etc., adheres to the moist vessels. Metallic iron is removed by a magnet. Small lots are ground by hand with a pestle and mortar of iron or wedgwood ware; on a larger scale the amalgam, or accumulated cleaning, is treated in a miniature iron tube mill, or a Knox or Berdan pan. The tube mill may be 2 ft. in diameter by 1 to 4 ft. long, with steel balls or rods of drill steel; it may be worked in batches through a covered hand hole, or continuously by a stream of water passing through hollow trunnions. The Knox pan is a small cast-iron pan with a muller carried on a vertical shaft; the Berdan revolves on an inclined shaft, grinding by means of two or three large balls, or by drags chained to a fixed post.

The amalgam is squeezed in fairly heavy (10-oz.) canvas; the finish is usually given by hand in balls of about 100 oz. each, or in cylinders compressed in a hydraulic machine with disks of canvas and coconut matting at each end; the removal of excess mercury is facilitated by heating the balls in hot water.

A high "percentage of retort" is favored by a large percentage of gold in the resulting bullion, coarseness of the original particles of native gold, frequency of clean-ups (giving mercury less time to penetrate), pressure applied in squeezing (much increased by use of machine), and high temperature during the squeezing. About 60 per cent is occasionally reached, while silvery amalgam may yield only 25 per cent; 35 per cent is about average for hand-squeezed amalgam.

Amalgam retorts are made in the pot form for charges up to about 2000 oz., and should be not over two-thirds filled. For larger amounts the cylindrical built-in form should be used, fitted with three or four light cast-iron trays. The trays or pot retorts are given an internal wash of wood ashes, fine clay, or chalk, or are painted with iron oxide, to prevent adhesion of bullion. Paper is sometimes used, but may cause flouring of the mercury. The covers or doors are best sealed with a lute made of sifted wood ashes and secured by well-driven wedge keys. A long condenser should be used, with a jacket supplied with cold water. In large retorts it is convenient to use loose dividing pieces of sheet iron, similarly painted, so that the resulting bullion will readily fall into pieces of convenient size for charging into crucibles.

Any convenient fuel may be used in retorting, and a pot retort may be heated in any style of melting furnace, or in the open if surrounded by a piece of sheet iron, but it is essential that the top be covered and kept hot, or the mercury vapor will condense before escaping. The temperature of boiling mercury is 356°C. (672°F.) and its latent heat 125 B.t.u. per lb. On account of the high specific gravity of the vapor (seven times that of air), the discharge pipes should point downward as far

as possible and means should be adopted to carry off any escaping fume and prevent its inhalation, especially if it is necessary to open the retort before it has time to cool. The mercury carries over a trifling amount of gold, most of which is due to spattering in the earlier stages of volatilization. The loss of mercury should be very small; any considerable difference in the weight of amalgam and of bullion plus mercury points to a defective lute or a leaky retort.

Bars of mill bullion or refined cyanide product are melted in graphite crucibles with borax sufficient to form a cover, and poured into iron molds previously smoked heavily or coated with graphite. About 2000 oz. is the usual weight limit for gold bars, and about 1000 to 1200 oz. for silver.

Bars containing gold and silver with little base metal other than copper suffer very little segregation and solidify rapidly. In sampling them it is safe to chip from one corner at the top and the opposite corner at the bottom or to drill ¼- or ⅜-in. holes at opposite corners. Cyanide bars containing lead or zinc are irregular in composition and should be sampled from the crucible just after stirring, or a sample may be taken while pouring by deflecting some of the flowing metal into a vessel of water.[1]

As soon as the bullion solidifies in the mold, the slag may be removed by pouring water on it and scraping it out, or by plunging the hot bar into cold water. Plunged bars retain a little water if the surface is rough.

CYANIDATION

Cyanidation.—At the present time sodium cyanide, NaCN, has entirely superseded potassium cyanide, KCN, as a solvent, and it alone will be considered here, although some metallurgists still make all calculations in KCN and recalculate the results to the actual salt used.[2]

The essential reactions of the cyanide process are, for gold,

$$2Au + 4NaCN + O + H_2O = 2NaAu(CN)_2 + 2NaOH$$

This is Elsner's reaction, verified by Maclaurin, indicating the necessity for oxygen or its equivalent. Metallic silver follows the same reaction, substituting Ag for Au. Cyanides of other alkali and alkali-earth metals act in precisely the same way, substituting Ca, Ba, 2K, etc., for 2Na. Hydrocyanic acid is an extremely feeble solvent, and cyanogen itself is without action on gold.

Silver chloride is rapidly dissolved, without oxygen,

$$AgCl + 2NaCN = NaAg(CN)_2 + NaCl$$

and most other silver compounds are similarly dissolved.

Silver sulphide, however, dissolves slowly, the reaction being reversible and requiring an excess of cyanide.

$$Ag_2S + 4NaCN \leftrightarrows 2NaAg(CN)_2 + Na_2S$$

Artificial gold sulphide is similarly dissolved. The solutions obtained always contain more or less thiocyanate (NaCNS), and this probably results from oxidation of the Na_2S.

$$Na_2S + O + H_2O + NaCN = NaCNS + 2NaOH$$

Free sulphur, resulting from partial oxidation of pyritic ore, or sulphur from thiosul-

[1] See Sampling, pp. 72, 76, 78, and 80 of the volume entitled "Principles and Processes."

[2] It is convenient to remember that, for all practical purposes, 4 lb. KCN = 3 lb. NaCN, and 1 lb. of 98 per cent NaCN = 2 lb. of Aero containing cyanogen equivalent to 49 per cent NaCN. Also that 10 cc of 0.5N $AgNO_3$ (8.50 g. per l) = 0.049 g. NaCN = 0.05 g. of 98 per cent salt, or 0.1 g. of Aero at 49 per cent.

phates formed by the action of lime or soda on pyritic ore, also reacts on cyanide with formation of thiocyanate.

$$S + NaCN = NaCNS$$

Tellurides of gold and silver are scarcely affected by cyanide solutions, and silver selenide is very slowly attacked.

ELECTROMOTIVE FORCE OF METALS IN CYANIDE SOLUTIONS[1]

Concentration KCN	Most probable value for e.m.f. Zinc	Copper	Gold	Silver	Lead	Mercury	Iron
6.5 per cent = N..........	+0.945	+0.930	+0.42	+0.34	+0.20	+0.15	−0.03
0.65 per cent = $N/10$.......	+0.870	+0.68	+0.265	+0.195	+0.16	+0.05	−0.09
0.065 per cent = $N/100$.....	+0.775	+0.43	+0.09	+0.055	+0.11	+0.04	−0.12
0.0065 per cent = $N/1,000$..	+0.415	−0.05	−0.34	−0.31	+0.07	−0.19	−0.13
0.00065 per cent = $N/10,000$..............	+0.385	−0.25	−0.45	−0.42	+0.05	−0.59	−0.14

[1] CHRISTY, *Trans. A.I.M.E.*, Vol. 30, pp. 921–922.

As calculated from the chemical equivalents, 1 lb. NaCN suffices to dissolve 1.1 lb. Ag or 2 lb. Au; 1 lb. Zn to precipitate 3.3 lb. Ag or 6 lb. Au. An ounce of metallic silver, therefore, requires 1.8 times as much of either reagent as an ounce of gold, and a dollar's worth of silver at the ordinary range of price uses forty to sixty times as much as a dollar's worth of gold. In practice, the difference is even greater because, as a rule, gold dissolves readily in dilute solution, while silver often occurs as the sulphide, which requires a stronger cyanide solution owing to the reversible character of its reaction. On the other hand, silver chloride dissolves rapidly and with little decomposition of cyanide.

Under identical conditions, metallic silver dissolves about half as fast as gold, or in exact proportion to their atomic weights. Silver-free gold dissolves more readily than gold alloyed with silver. Maclaurin showed that all gold-silver alloys should dissolve in cyanide solution at the same rate as measured in thickness removed, and in the same proportions in which they exist in the original alloy; Yokobori and others confirm this.

As regards the effect of amalgamation on the rate of dissolution by cyanide, some contrary evidence has been adduced. In stationary beaker tests with pure gold foil, a mere film of amalgam retards solution about as much as thorough wetting with mercury—similar pieces show one-half to one-tenth the rate of solution noted with clean gold; when agitated in sand mixtures the same tendency is noted.

For a given percentage of NaCN, gold in a thick slime mixture dissolves much less rapidly than in thin pulp, the same is true of silver, of oxygen, and of salts such as NaCN itself—lumps of which should not be dumped in agitators but predissolved in clear solution or water. This effect seems to be partly due to the greater viscosity of thick pulp, partly to the smaller proportion of solution to unit volume and unit surface.

After a certain period of contact with a given solution, the dissolution of gold from ore practically ceases, in spite of agitation and ample aeration; on adding fresh solution, or replacing a part with barren solution or even with water, further dissolution takes place. This is more marked with silver than gold, and especially on adding

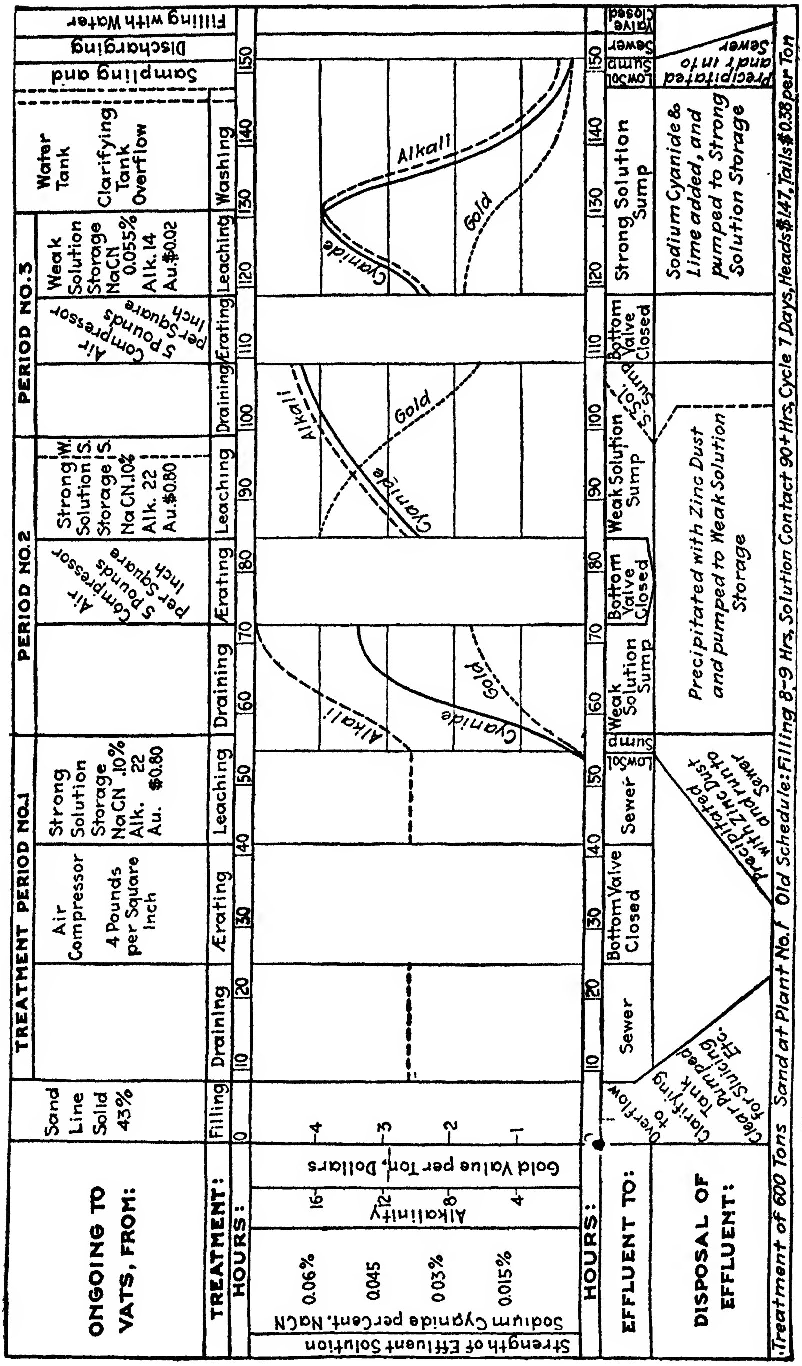


Fig. 5.—Leaching at Homestake, S. D. See Clark and Sharwood, *Trans. I. M. M.*, **22**, 68.

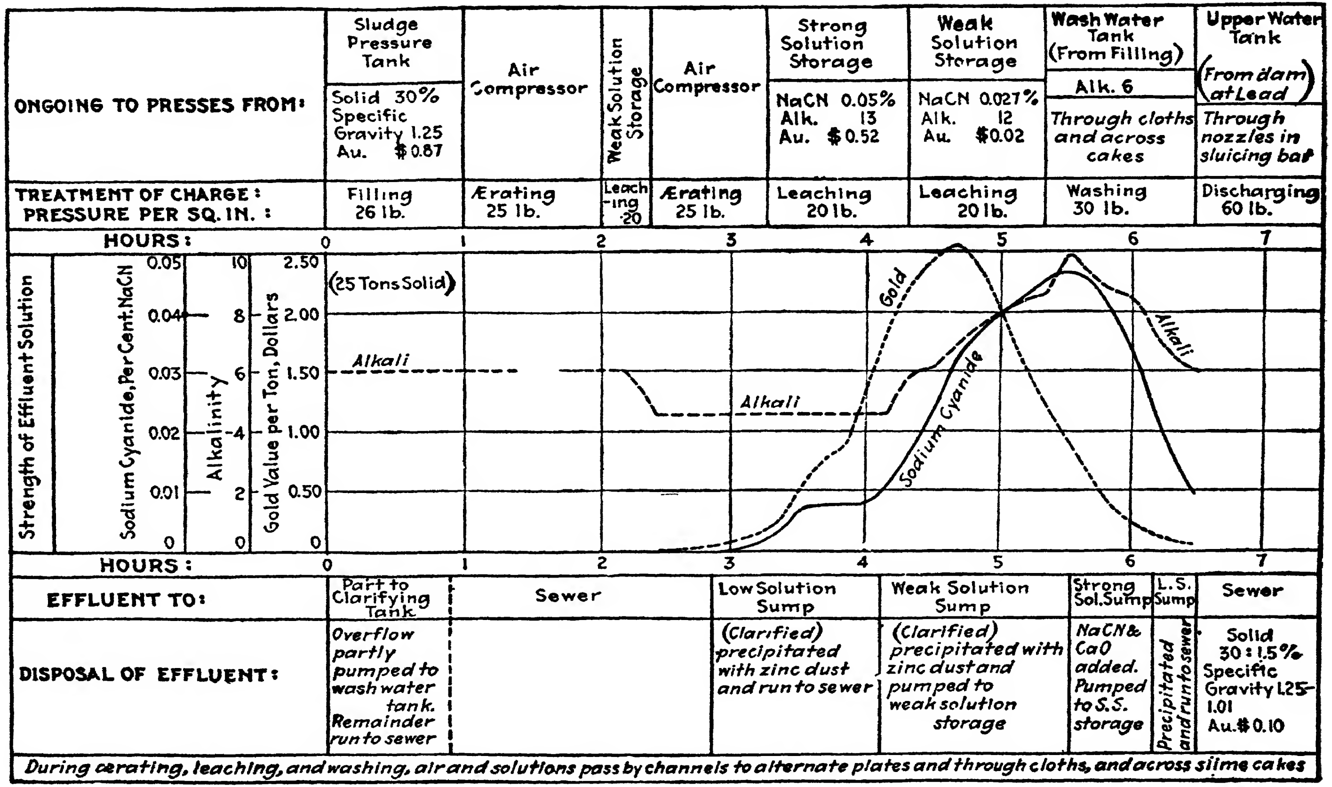


FIG. 6.—Slime treatment in Merrill filter presses at Homestake, S. D. See CLARK and SHARWOOD, *Trans. I.M.M.*, **22**, 68.

aerated barren solution from extractors. Some of the effect is, no doubt, due to the inert or "fatigued" solution having reached an equilibrium with the ore, but probably much of the later apparent dissolving is actually diffusion of the richer solution adsorbed or absorbed by the ore particles.

In sulphide ores, especially complex sulphosalts, silver may be very slowly soluble; this may often be partly overcome by removal from the solution of the Na_2S formed by means of lead compounds; mercury salts are sometimes used with advantage, and fine grinding is essential. Owing to the reversible character of the reaction with Ag_2S, a short treatment with very strong (1 per cent or more) solution of NaCN is often much more effective than long treatment with dilute.

The best strength of solution must be determined by experiment. In agitation systems, coarse gold being removed if originally present, slime may be treated with solution of 0.1 to 0.01 per cent NaCN; silver slime may require 0.2 to 0.5 per cent or higher.

In well-roasted sulphide ore or concentrate the gold is, as a rule, amenable cyanide, but the globular particles from roasted tellurides dissolve slowly; silver in similar roasted material becomes partly insoluble; extremely fine grinding is desirable with most rich silver material. After fine grinding, such material is sometimes put back in the same circuit with average ore; it is best first to give it a separate intensive treatment with strong solution.

Gold telluride ores must be either roasted or treated with some oxidizing agent, such as bromocyanide, BrCN, after preliminary leaching; or any alkaline bromate, or peroxide of sodium or barium, may be used after preliminary treatment with NaCN.

Many other oxidizing agents have been tried in connection with cyanide treatment, to supply "nascent CN" or its equivalent, but none has been able to compete with atmospheric oxygen for ordinary ores.

Lead and Mercury in Cyaniding.—Mercuric oxide and chloride dissolve completely in cyanide solutions

$$HgO + 4NaCN = Na_2Hg(CN)_4 + 2NaOH$$

but when mercurous oxide or chloride is treated with alkaline cyanide, half the mercury remains insoluble in the metallic state.

$$2HgCl + 4NaCN = Hg + Na_2Hg(CN)_4 + 2NaCl$$

An old tailing pile containing HgCl, therefore, cannot be expected to yield 50 per cent of the mercury by cyaniding; mercuric oxide would give an almost complete recovery; the sulphide and metallic mercury would yield little or nothing.

Lead is sometimes added to solutions as the acetate (54.6 per cent Pb) or nitrate (62.56 per cent Pb), the latter being generally more economical. Litharge (PbO = 92.8 per cent Pb) is sometimes added to grinders, or ground with lime. In alkaline solutions the lead is dissolved as plumbite, Na_2PbO_2, which reacts with sulphides to form PbS. Occasionally, a local oxidized lead ore ($PbCO_3$) has been similarly used. Removing Na_2S, lead facilitates the solution of Ag_2S, argentite, but it has no beneficial effect on the complex sulphosalt ores of silver. Mercury would similarly precipitate the sulphide radical as HgS. Both lead and mercury also influence precipitation. Contact with zinc dust or shaving at once throws down metallic lead or mercury, forming a zinc-lead or zinc-mercury couple which facilitates precipitation of gold and silver, and is especially advantageous when zinc shaving is coated with copper. Lead added to solutions at the time of precipitation is found in the precipitate, and is sometimes troublesome in refining unless cupellation is practiced. Any mercury in solution is similarly precipitated, and when zinc precipitate contains much (say 10 per cent) of it, its removal by distillation may be profitable.

Losses of Cyanide.—Losses of cyanide are mechanical and chemical. The first comprise the cyanide that is carried off in solution, some of which may be unavoidably thrown away daily, to prevent accumulation of too great a volume, or may be discharged in the residue, the washing of which is necessarily imperfect.

Chemical losses include that due to hydrolysis of NaCN ($2NaCN + H_2O = 2NaOH + 2HCN$), but this effect is slight in solutions that are distinctly alkaline, and is much smaller in old solutions [which often carry most of their CN in the form of $Na_2Zn(CN)_4$] than in simple NaCN; decomposition of NaCN by acids, including CO_2 contained in air used in agitation ($2NaCN + CO_2 + H_2O = Na_2CO_3 + 2HCN$); oxidation of NaCN by oxygen of air to form NaCNO and other inactive compounds, such as bicarbonates ($NaCN + O = NaCNO$; $2NaCNO + 3H_2O = Na_2CO_3 + 2NH_3$, etc.); reaction with iron compounds, copper, etc., to form Prussian blue and various double cyanides, and with sulphur to form NaCNS.

Cyanicides.—"Cyanicide" is a convenient name applied to all those substances found in ores and tailings which cause a loss of the essential ion CN from the solutions used in treatment. Under this head may be grouped acids that directly decompose NaCN (including carbonic and humic acids); salts such as sulphates and arsenates, especially those of iron, which consume free alkali [$Ca(OH)_2$ and NaOH], thus facilitating the hydrolysis of NaCN; ferrous salts and oxidized compounds of copper and zinc which form complex cyanides, either entirely inert or feeble solvents for gold and silver; and certain sulphur compounds that react with NaCN to form NaCNS.

When used injudiciously and in excess, even oxygen, chlorine, bromocyanide, peroxides, and other oxidizing agents are actually cyanicides. The cyanide actually used in dissolving gold is almost negligible, but rich silver ore consumes more—100 oz. of silver using over 6 lb. NaCN to form the double cyanide.

Copper in oxidized ores is usually in the form of the green or blue carbonate (malachite or azurite), an oxide, basic sulphate, or occasionally the metal. In pan-amalgamation tailings it occurs in similar forms from decomposition of added sulphate. In all these forms it is readily dissolved by cyanide solutions and decomposes or renders useless approximately three times its weight of NaCN, or four times of KCN. In the case of KCN, the actual cuprous compound formed appears to lie between $K_2Cu'(CN)_3$ and $K_3Cu'(CN)_4$, while a portion of the CN is oxidized to CNO in reducing combined Cu'' to Cu'. As little as 0.1 per cent of soluble copper may, therefore, cause a loss of several pounds of cyanide per ton treated. Unoxidized suphide ores are commonly but little attacked and decompose relatively little cyanide.

From some oxidized ores it is possible to remove the soluble copper by dilute ammonia, or, if but little calcium carbonate is present, by dilute sulphuric acid; in either case the dissolved copper must be removed by thorough washing before contact with cyanide solution.

Iron and steel in the form of sheet metal, etc., are practically without effect on cyanide solutions. Some writers have insisted that the fine metallic iron introduced into ore by wear of mill castings, steel balls, and rods, etc., which may range from 1 to 5 lb. per ton, decomposes cyanide and interferes with gold extraction. In practical tests, it is difficult to recognize any losses due to metallic iron as such. Any actual decomposition is probably due to ferrous compounds produced by oxidation of this finely divided metal, or by the action on it of acids resulting from oxidation of sulphur compounds in the ore.

Antimonial Ores.—Ores containing antimony as sulphide (stibnite) have, in some instances, given trouble in extraction, and also by yielding an impure precipitate, difficult to refine unless cupellation is practiced.

Fine grinding has been recommended, and the use of a solution as low as possible in cyanide and especially low in free alkali. In other cases some success has been

reported in the adoption of a treatment with comparatively strong solution of sodium hydroxide or sulphide to dissolve interfering antimony compounds, and washing out the solution before cyaniding.

In some antimonial ores, as with others containing Se or Te, all or most of the gold may resist both amalgamation and cyanide, and may also be impossible to concentrate. A thorough roast, followed by fine grinding, generally renders a high percentage soluble in cyanide solution.

Arsenical Ores.—Many of the common arsenical minerals, notably arsenopyrite, FeAsS, are totally unaffected by cyanide solution; their oxidation products are, however, soluble in many cases. When arsenic passes into solution, some of it may appear in the precipitate, and in this case extreme precautions must be taken in disposing of the fumes from acid treatment, which may contain arsine, AsH_3.

The presence of manganese minerals in gold ores appears to have no ill effect in cyaniding; some silver ores contain large percentages of manganese peroxide but yield readily to cyanidation; others, some of them containing relatively small proportions of manganese, yield only a small percentage of their silver, even to strong cyanide solutions. Mere addition of MnO_2 has no prejudicial effect, and it is probable that in the latter ores a more or less definite manganite of silver exists, analogous to the compounds of barium and copper found in psilomelane. Investigations by R. Linton, E. M. Hamilton, and W. H. Coghill show that in some cases treatment with dilute hydrochloric acid, salt and sulphuric acid, sulphur dioxide, hydrogen sulphide, or a sulphydrate, or a chloridizing roast leaves the silver in a form permitting a high extraction with cyanide solution, though it may be insoluble in nitric acid. Reagents that decolorize the dark manganese compounds generally free the silver.

For instance, Hamilton, in one case, extracted only 5 to 15 per cent at 200 mesh, additions of lead, oxidation, hot solutions, chlorine, and sodium sulphide, Na_2S giving no improvement. A preliminary treatment with H_2S or NaHS increased the extraction to 73 per cent, HCl to 94 per cent, 5 per cent SO_2 to 84 per cent, and a chloridizing roast to 75 per cent, when followed by agitation with dilute KCN solution. Concentration, oil concentration, and flotation gave no results.

The Caron process commences with a "reducing roast" to decompose peroxides, and in certain cases has greatly increased the subsequent extraction of silver.

Calcium sulphate is sometmes an original constituent of ores and tailings and of some waters; more commonly it results from the roasting or weathering of calcareous ores containing sulphides, and occasionally from the action of sulphuric acid on such ore. Lead sulphate may also react with limey solution to give a saturated solution of $CaSO_4$. In Colorado and Western Australia, leaching of roasted ore has sometimes been followed by the setting of charges to a cementlike mass, which might require blasting. A more common result is the supersaturation of cyanide solutions with $CaSO_4$, which crystallizes as a hard deposit on pipes, canvas, etc., and may coat zinc shavings so as to render them inactive. A complication is caused by the fact that the solubility of $CaSO_4$ in water decreases with a rise of temperature.

Magnesium sulphate may be similarly formed; while readily soluble, it is equally objectionable owing to the flocculent precipitate formed when its solution is mixed with another differing in alkalinity.

Owing to the presence of carbonaceous matter (not graphite) in black schists associated with the ores, it has been impossible to secure good extractions of gold at certain mines in various parts of the world, much of the gold being reprecipitated as soon as dissolved in some form which has never been positively identified, though much has been written on the subject. Charcoal from charred mine timbers, etc., similarly interferes.

In the case of some African ores, a process was worked out by Feldtmann and Wartenweiler for extracting the reprecipitated gold by a subsequent leaching with sodium sulphide solution.

A more recent method is that of Silver and Dorfman, who give the ore a preliminary agitation with a little flotation oil, which prevents the carbonaceous matter from interfering.

Some pyritic concentrates oxidize rapidly to $FeSO_4$, etc., and then decompose large amounts of NaCN, forming ferrocyanides, Prussian blue, etc. This may be obviated by a fairly long aeration in the presence of lime or soda, oxidizing the iron completely to ferric hydroxide.

At the Goldfield Consolidated mill the concentrates contained copper as well as iron sulphates. Soluble copper and iron were removed by preliminary treatment with dilute sulphuric acid, followed by an alkaline wash, after which the fine-ground concentrate was cyanided in a Pachuca tank with repeated decantation, finishing in a Kelly filter.

Lime is used in cyaniding to neutralize acid existing in ore, or the "latent acidity" of such salts as basic ferric sulphate, thus protecting cyanide from decomposition. It is also of value in increasing the settling rate of slime.

When crushing in water, quicklime may be fed dry with the ore, or may be slaked or ground in a tube mill or pan. This early introduction effects neutralization at the earliest possible stage, but sometimes has an adverse influence on amalgamation. It is advisable when crushing in cyanide solution. An opposite policy is followed at the Homestake sand plants, where the ore develops acidity by oxidation and a granular lime is required for progressive neutralization; here it is crushed by a stamp through a seven-mesh screen and mixed with the sand just as it passes to the collecting-leaching vats.

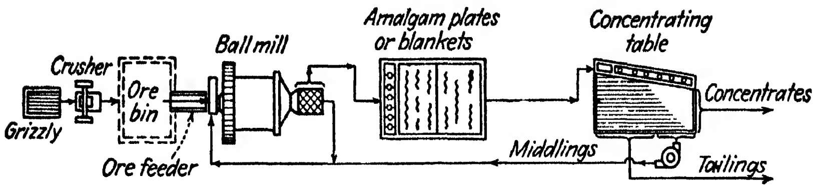
In treating dry sand, the lime should be slaked carefully, and the fine product mixed as uniformly as possible with the charge at any convenient stage. With slime pulp, it may be used as milk of lime fed from a grinding pan or mixer. Acid and bicarbonate waters consume an appreciable quantity of lime. In some cases, as when aluminum is used as a precipitant, the calcium in solution must be replaced by sodium, by the use of caustic soda or soda ash.

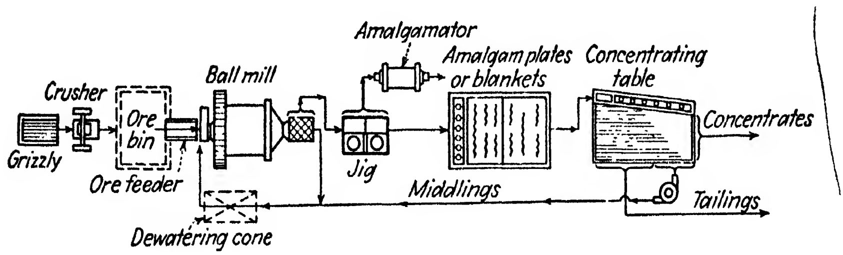
An excess of alkali in solution protects NaCN from hydrolysis, but it usually retards and may even prevent the dissolving of gold and silver, especially with sulphide ores. Alkalinity must, therefore, be carefully controlled, and it is generally best to maintain it at the lowest possible point in excess of that corresponding to the cyanide (NaCN) indicated by titration—in other words, the protective alkali should be as near to zero as possible. This is generally safe, as old solutions containing zinc show little tendency to hydrolysis of HCN.

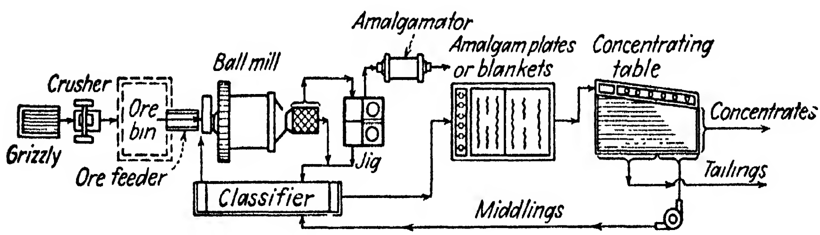
Lime should be free from charcoal and contain but little magnesia. The available CaO in good quicklime is between 80 and 90 per cent; it is easily determined by shaking 2 g. with 20 g. of sugar in 200 to 1000 cc. of distilled water, and titrating one-twentieth of the clear liquid with standard acid.

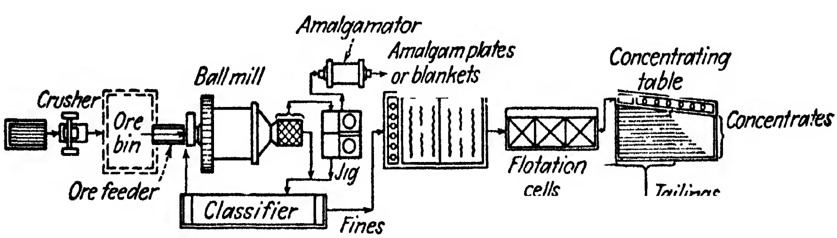
Sand and Slime.—In the first MacArthur-Forrest patents, agitation in cyanide solution is indicated, but in the early practical plants some form of separation was found necessary, the coarser material, including as much of the fines as possible, was leached, the "slime" being allowed to accumulate untreated, unless exceptionally rich.

"Slime" properly refers to colloidal material—"superfine particles"—which can be neither leached nor settled readily; Gross has defined it as "anything which renders water muddy." The slime separated by classification is largely extremely fine sand, the microscope showing this to consist of crystalline particles. Leachable sand









Figs. 7–10.—Typical flow sheets of successful gold-milling installations:[1] 7, simple flow sheet for high-grade, free-milling ores; 8, an added jig and amalgamation unit give additional recoveries; 9, a classifier in closed circuit increases the grinding and jigging efficiency; 10, flotation cells recover sulphides formerly lost.

[1] These flow sheets furnished by the Denver Equipment Co., Denver, Colo.

may contain 40 or 50 per cent of material finer than 200 mesh, provided true (colloidal) slime is practically eliminated. In general, quartz and pyrite tend to pass into sand during classification, while the slime contains the more basic and hydrous constituents of the ore—especially limonite, and hydrous silicates of alumina and magnesia, such as kaolin and chlorite.

In rare instances, a porous ore, containing no coarse gold, may be crushed coarsely (to, say, ¼ in.) and leached directly, but classification is more generally necessary.

"All-sliming" is a term loosely applied to the comminution of an ore to pass 200 mesh—sometimes extended to 100, or even 80 mesh—the general idea being to ensure a product that can easily be kept in suspension.

Crushing in cyanide solution was first attempted by A. B. Paul in California, but was little used until 1899; since then its use has rapidly increased. Milling in water washes out soluble cyanicides, and lime may be used to neutralize latent acidity, in some cases saving much cyanide; amalgamation may be thus kept in advance of contact with cyanide. Crushing with cyanide complicates the sampling of heads, owing to dissolved values, but has many advantages, dissolution of gold beginning as soon as the ore enters the mortar or mill, and the only water introduced into the system being original moisture and that used as a final wash. From 50 to 75 per cent of the soluble gold may dissolve during milling, but with silver, solution is much slower.

Sand Leaching.—Sand is leached in vats with filter bottoms, filtration being effected by gravity, in some cases aided by the application of a vacuum beneath the filter. The vats are cylindrical, of steel or wood, redwood or cypress being generally preferred on account of their durability. They must be made absolutely watertight, with substantial foundations, preferably parallel walls of concrete arranged to allow of easy inspection of the bottom and sides. Vats of reinforced concrete have been used, of various shapes, made tight by the use of bituminous coatings. Wooden vats should have the staves doweled, bottom boards either doweled or grooved for the insertion of pine tongues, and bottom end joints made with metal tongues. The bottoms should have a slight slope toward the solution outlet.

Filter Bottoms.—A ring of wood is placed around each bottom, about 1.5 in. from the staves or side, forming an annular channel for the rope used to secure the stretched filter; the height of this varies, but should be 3 to 5 in. for large vats. The space inside this ring is occupied by some form of wooden grid of equal depth. One of the best forms is a system of parallel strips, set edgewise and notched or crozed on the under side for half their depth so as to allow of free circulation. For instance, the strips may be 2×4 in. or 2.5×5 in. with notches 4 or 5 in. long and 4 or 5 in. apart; the strips themselves are nailed down 2 or 3 in. apart. A similar effect is produced by continuous 2×2 in. strips laid parallel and resting on similar but short pieces 6 in. apart, laid crosswise on the bottom with spaces between their ends; or the parallel strips may rest on short blocks through which the nails pass.

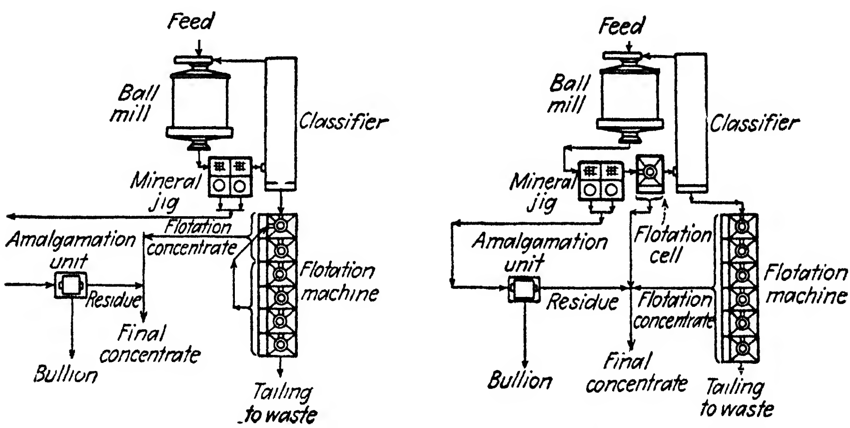
Upon the strips is laid a circle of coconut matting, sewn and hemmed, and fastened on the ring by occasional nails or staples. Over this is the filter proper, of heavy canvas, cut somewhat larger than the tank bottom, tightly stretched, and fastened by driving an inch rope into the recess round the tank bottom. In South Africa, hessian (burlap or hop cloth) has been laid on the wood grid, and coconut matting above this. When vats are discharged by shoveling, the upper cloth must be protected by boards, say 6 in. wide and a few inches apart, or by wider boards with numerous holes 1 in. or larger.

Around bottom discharge doors a tight wood ring is built up, of the same height as the filter. Near solution outlets all approaches must be kept clear. Near such outlets it is well to have a movable false section of bottom, which can be lifted occasionally to remove accumulated fine sand which may pass through holes in the filter. The

canvas filter should have a valve or opening, which can be closed by tying a sleeve sewn into it, to release air when the water is introduced.

Discharge Openings for Sand Residues.—These may be placed in the bottom of the vats or in the sides close to the filter bottom. In the latter case some of the hoops or rods for wooden vats must pass round the gate frame, or connect with the frame. Sluicing gates in the bottom should be near the sides, with one in the center of a large vat; for shoveling they should be so distributed that each serves a nearly equal area, but they should also be placed in straight lines so grouped as to require a minimum number of car tracks or sewers beneath the vats.

Side doors are rectangular; bottom doors may be round; they open outward and are conveniently hinged, and secured when closed by swing bolts or by a hinged lever arm tightened by a swing bolt. They may be of pressed steel or cast iron, made tight by square packing. A convenient center gate is that of Merrill, closing tight



FIGS. 11–12.—Typical flow sheets of successful gold-milling installations:[1] 11, a simple flotation plant with a jig recovers metallics in the grinding circuit; 12, the jig recovers non-floating minerals, and the unit flotation cell following it recovers a coarse bulk concentrate and reduces slime losses.

an iron ring, and lifted from above by a threaded central rod in a column of pipe; the latter may also serve as support for a movable Butters distributor. To diminish resistance in lifting, such bottom valves should be made with the top an acute cone.

Leaching vats may be filled with current mill pulp, or with dam sand, conveyed by water or solution, or with dry sand or crushed ore. The main consideration is to secure uniform distribution and uniform permeability. If loaded wet, the vat should be first filled, or at least partly filled, with water or solution.

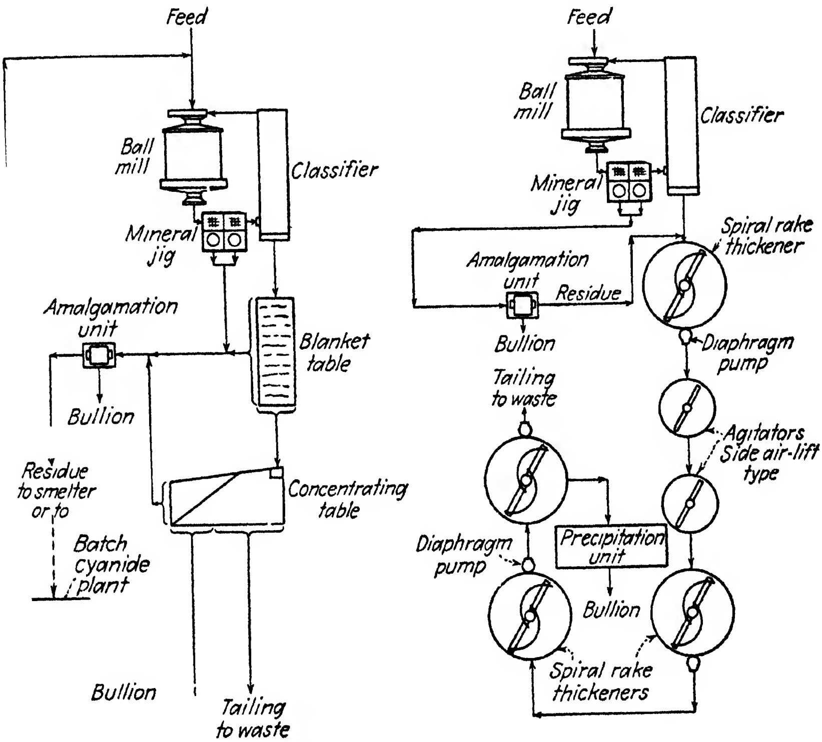
The total overflow during filling = original water + conveying water − interstitial space in charge = original water + total volume pulp fed − net volume of sand in charge.

Wet sand is usually fed through a Butters-Mein distributor (the revolving lawn-sprinkler type) with six or eight arms of 1½- or 2-in. pipe of differing lengths ending in elbows with flattened lips. For uniform filling the tank bottom is divided into equal annular areas, each radial pipe terminating nearly over the middle of a ring. The overflow is carried off by an annular launder, usually outside the staves, but sometimes built inside. With cheap labor, as in Africa and Mexico, filling was often done by a man with a hose.

[1] These flow sheets furnished by the Denver Equipment Co., Denver, Colo.

As soon as filled, the sand is allowed to drain, and solution is applied to the top; it may be applied as a spray or allowed to pour upon the sand—in the latter case sheet-iron pans are used to prevent washing holes in the surface.

In filling with dry or drained sand, conveyers may be used—a main belt running along or between rows of vats, with a traveling shuttle belt across the vats—with automatic discharge. Or the feed may discharge over the center of the vat and slide down a radial inclined shoot with adjustable openings, the shoot being gradually



FIGS. 13–14.—Typical flow sheets of successful gold-milling installations:[1] 13, a small batch cyanidation plant may be used to obtain all-bullion products; 14, a jig removes coarse gold ahead of cyanidation, improving recovery and eliminating erratic tailings.

moved round the vat by hand. Or barrows, cars, etc., may be simply dumped over a coarse grating supported just above the top of the vat.

When filling with dry or drained sand, some hours of treatment time may be saved by simultaneously introducing solution below the filter bottom, so that it rises through the sand about as fast as the sand accumulates. As soon as the vat is filled and solution reaches the top, the bottom supply is cut off and normal downward leaching is started.

Direct treatment in the same vats in which sand is settled wet is only practicable when colloids are absent or have been washed out almost completely by cones, *Spitzkasten*, or other classification systems. Filter-bottomed collecting vats are sometimes used, and may be superimposed above the treatment vats, the settled sand being transferred to the latter by shoveling or by an excavating machine, such as the

[1] These flow sheets furnished by the Denver Equipment Co., Denver, Colo.

Blaisdell. Instead of an annular overflow launder for the collecting tank, vertical slots have been used in Africa for overflow water outlets, the outflow level being automatically raised by roller-blind devices carried on floats, or it may be raised by cast-iron rings placed above a bottom opening.

In double treatment, the sand is collected and drained in such tanks, and given a preliminary cyanide solution treatment to displace the water; it is then transferred to the treatment vats below, where leaching is completed. The aeration thus secured is beneficial.

Caldecott's continuous-collecting system for sand consists in classifying with diaphragm cones and draining the thickened sand on a slowly revolving horizontal table, about 20 ft. in diameter, provided with a wide annular filter of coco mat and calico supported on wire screen. Here the sand is dewatered by a vacuum of about 5 lb. per sq. in. and removed by a fixed plow; it falls on a belt conveyer and is convey to the treatment vats.

Leaching.—The manner of applying solution varies. Gold dissolves rapidly, especially from fine sand, giving rich effluents in the early stages of leaching, th value falling off rapidly; silver often dissolves slowly, showing less difference in th value of the effluents with time. For instance, a particular ore yielded 70 per cent of the extractable gold, but only 35 per cent of the extractable silver in the first quarter of the total effluent solution. Hence, by precipitating only the first half of the effluent, and using the later portions fortified in cyanide for the early treatment of succeeding charges, the volume precipitated is minimized, so that it may be possible to make good extractions while precipitating not more than half a ton of solution per ton of sand.

The strength and the alkalinity of solution and the number of hours of contact must be determined to suit each case, and great saving may result from adjusting these conditions, and the degree of comminution of the ore, after the general treatment has been established.

When two solutions are used, the strong is generally applied first, and the weak is followed by wash water sufficient to displace it. The wash water and water in moist or water-crushed ore mix with the solutions to some extent, yielding "first and last drainings" of low NaCN content and low in precious metals. To preserve the volume of plant solution constant, these drainings, or low solution, are best precipitated separately and the barren run to waste. A slight saving is effected by using a buffer of this barren solution just before the wash water. Sometimes a little weak solution is similarly used before the strong; this is advisable if cyanicides have not been removed previously.

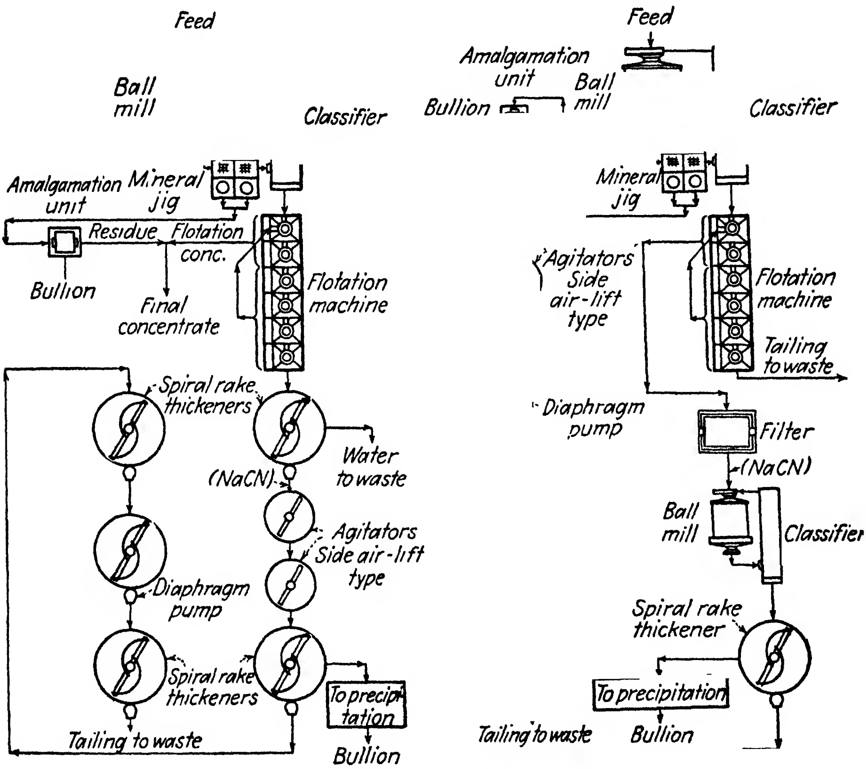
When dry ore is crushed in cyanide solution, the final wash water must be regulated to make up the deficit in solution that would occur otherwise.

The "leaching rate" of sand is measured by the fall per hour in the surface of solution standing over a charge of saturated ore in the vat. Good extractions are usually obtained with leaching rates of 2 in. or more per hour; at 1 in. more care is necessary, and slower rates are generally dangerous, shortening the time of contact by reason of the longer washing period necessary. As the voids in settled sand are usually about 50 per cent of the volume, solution descends through sand at about double the surface leaching rate, and the hours required for displacement of solution by wash water may be approximated by dividing twice the surface rate into the inches depth of charge.

With sand of given character, the leaching rate is not much retarded by a moderate increase in depth; the effect of depth is largely offset by increased head. An extremely thin layer of slimy material may, however, affect the rate profoundly. Application of a vacuum beneath the filter bottom was formerly practiced, when classification was

usually imperfect; while increasing the flow it tended to cause packing of the charge and lower the normal leaching rate; it may be used with advantage in the final washing stages.

Solution may be supplied continuously to the charge, or may be added at such intervals as to allow the surface to become drained and thus entrap air. Solution is sometimes circulated repeatedly through a charge by an air lift or pump returning it from the bottom to the top; this gives the desired aeration, but the ultimate removal of precious metal is retarded. Maceration or soaking by closing solution outlets for



FIGS. 15–16.– Typical flow sheets of successful gold-milling installations:[1] 15, combination flotation and cyanidation permits milling both oxides and sulphides; 16, cyanidation of flotation concentrates produces all bullion.

long periods is an obsolete practice, but a too rapid flow should be controlled to avoid precipitating unnecessary solution.

Tanks.—For economy of material a round tank of uniform thickness should have a depth equal to one-half the diameter, for economy of hoops the shallower the better, for economy of foundation the reverse. A common compromise is to make the depth one-fourth to one-sixth the diameter. In steel vats the bottom is usually at least $\frac{1}{16}$ in. thicker than the sides; these also may be lighter toward the top. Steel tanks are riveted and have a ring of angle steel surrounding the bottom; a similar ring is often used at the rim, and deep tanks may be stiffened by a ring of T iron or a channel section round the middle. For wooden tanks, round iron or steel hoops are preferable to flat ones, which often develop rust on the underside.

[1] These flow sheets furnished by the Denver Equipment Co., Denver, Colo.

To get the full strength, the ends should be suitably upset before threading, and the section at the bottom of the thread considered in calculating strength. For sizes requiring over 1⅛-in. round it is preferable to use 1⅛-in. or larger square steel. The sizes may increase by ⅛ from ½ in. at the top, and the spacing be made correspondingly closer as depth increases. Heavy hoops and rings must be rolled to the proper curvature before use, and hoops must be provided with properly designed couplings.

In calculating the necessary cross section of hoops or thickness of side, wet sand, like slime pulp, must be considered as a perfect fluid, as there are times when it is dangerously near that condition. Settled sand may be assumed to have 50 per cent voids, when the specific gravity of the wet mixture p is $0.5(d + 1)$ where d = specific gravity of dry sand.

D = diameter of tank in feet.
H = depth from top to center of ring (or hoop) considered, in feet.
p = specific gravity of pulp [$= 0.5(d + 1)$ for wet sand].
t = thickness of steel vat in inches at depth H.
W = inches width of ring controlled by hoop in wood vat at depth H.

Strain on square inch cross section of steel sheet $= \frac{2.6DHp}{t}$ lb.

Total strain on cross section of hoop $= 2.6WDHp$ lb.

Thus, with a steel tank 50 ft. in diameter, the metal ¼ in. thick at a depth of 10 ft., when filled with wet sand of specific gravity 2.8(p = 1.9), stands a strain of

$$2.6 \times 10 \times 50 \times \frac{1.9}{0.25} = 9880 \text{ lb. per sq. in.}$$

Similarly with a wooden vat under the same conditions, a hoop 10 ft. from the top, spaced 6 in. from adjacent hoops, is subject to a strain of

$$2.6 \times 6 \times 10 \times 50 \times 1.9 = 14{,}820 \text{ lb.}$$

and for a factor of safety of 5, the hoop must be capable of standing 74,000 lb.

Leaching in the Filter Press.—This includes collection and complete treatment in the press, and usually requires solution to be applied under a pressure of at least 30 lb. per sq. in. Separated slime or all-slimed ore, suitably thickened, is fed into the press by gravity, monte-jus, or pump, until filled. Alternate plates are then connected with compressed air and the water displaced. Solution is next applied through the same channels, and leaching (which may involve several solutions and may be alternated with air treatment) is continued as long as gold dissolves; it is then displaced by wash water, and the solid is finally discharged.

The Dehne press, used in Western Australia for roasted ore and in some cases for raw slime, was opened and discharged by hand; it did not differ essentially from the ordinary plate-and-frame press. Treatment was completed in some cases in a 2- or 3-hr. cycle, but operation was expensive, even when opening and closing were effected by hydraulic power, and it was generally found preferable to dissolve the gold in agitators and use the press for filtering and washing only.

The Merrill press discharges the solids by mechanical sluicing through a bottom channel provided with ports, making it possible to use a press continuously for many months without opening or changing cloths. Sluicing is effected by a series of nozzles in a rotating pipe or bar running the full length of the press and requires 3 to 5 tons of water per ton of solid, depending on the character of the latter; much of this water may be recovered, if desired, by a thickener or rotary filter. While the first cost of this filter is comparatively high, the treatment requires a minimum of labor. With granular slime, a 4-in. frame is suitable; if extremely fine or flocculent, a 2- or 3-in. cake is preferable. Center washing may also be used, in which case the cake is not

made to fill the frame completely, and air and solution are applied through the central opening in each cake instead of passing crosswise through the frame. In this case the cake is loosened by applying air for a short time behind the cloths prior to sluicing.

Leaching in the press is essentially similar to gravity leaching of sand, but much more rapid, occupying hours instead of days. For instance, with Homestake ore, the coarser mill sand yielded 70 per cent of its gold by leaching in a 7-day cycle; if reground this yield increased to about 80 per cent, the finer portions of the sand yielding 90 per cent. The slime and fine sand treated in the Merrill press yield 90 per cent in a cycle of 8 to 10 hr., of which 1 hr. is consumed in filling and one in sluicing. The operating cost in each case is about the same.

The Sweetland press has a cylindrical shell, opening by a hinge, the circular plates being tipped for discharge.

Simple Decantation.—In this process of slime treatment the material was agitated with cyanide solution and allowed to settle; the clear supernatant liquid was decanted off by a swinging pipe or flexible hose supported by a float that kept the inlet near the surface. This liquid was replaced by barren or low-grade solution or water; mixing, settling, and decantation were then repeated, and the same cycle might be repeated several times. The first decantate was always precipitated, sometimes the second or third, and the barren solution used with later decantates or washes for the make-up on a succeeding charge. The thickened residue, including more or less low-grade solution, was finally run off to a dam, or in some instances filtered. Some liquid separated on the dam and was sometimes pumped back for use in washes.

Successive agitations were carried out in the same vat—using mechanical agitation often aided by air—or, in a series of vats, one for each stage. In the latter case time was saved by hydraulicking the settled slime with solution or running it by gravity into a vat already containing solution, or, if the vats were on a level, a centrifugal pump was used with arrangements for drawing in a certain proportion of air for oxidation. Lime was commonly added to facilitate settling.

The process was adaptable to existing shallow vats by addition of an arm or paddle agitator. In South Africa, large shallow vats were used with bottoms slightly coned, but it was found that, with increased depth, air agitation could be advantageously substituted, and this led to the development of the extremely deep Pachuca tank by F. C. Brown at Komata Reefs, New Zealand, in 1902.

The Pachuca may be 10 × 30 × 45 ft., with a central air lift one-tenth the diameter and a cone bottom inclined 60 deg. In addition to the lifting air, a second small pipe was added for stirring settled slime, and later a spider or movable set of radial pipes surrounding the air lift for the same purpose. The air outlets were valved or covered with flexible rubber to prevent entry of slime when the air was cut off.

At Waihi the Brown vat was used for crushed ore in connection with the Moore filter; at Goldfield and Treadwell it was used for fine-ground concentrate, and the final removal of solution was effected with a Kelly filter press.

Continuous or series treatment (not to be confused with countercurrent) was first used by Grothe and Mennell in 1908. The cyanide pulp is transferred through a series of three to six Pachuca tanks, maintaining it in agitation, thus saving the time occupied in emptying and filling, settling and stirring, and avoiding loss of head, except a few inches between successive tanks. The connecting pipes between adjacent tanks are set at a downward angle of about 60 deg., with an intermediate section of rubber hose. After leaving the agitation system the pulp passes to a suitable filter, an intermediate storage tank being usually provided in advance of the Moore and Butters filters, which have been much used. This is unnecessary with rotary filters, which are automatic and almost equally effective.

By keeping the outlet at a suitable distance from the surface, any considerable accumulation of sand is prevented; a certain accumulation of sand in the system is desirable, giving the coarser particles a longer treatment time than the average. Shallower agitators, as the Dorr, Trent, or Parral, may be used; the discharge may also be selected by other means. Short circuiting of some particles must inevitably occur, but in a series of tanks the probability of this is decreased.

The intermittent vacuum filters (Moore, Butters, etc.) and pressure filters (Burt, Kelly, etc.) require more attention, but are more flexible in application, as treatment can be completed in them, as well as washing and dewatering; rotary vacuum filters (both the drum type, Oliver, and Portland, and the American or disk type), are practically restricted to washing and dewatering. Dewatering may be carried by any of these filters to about 25 per cent moisture.

In the Kelly system the agitators are followed by two sets of rotary washing filters in series; the cakes discharged from the first set are repulped with wash solution or water in intermediate mixers to a liquid ratio about 1:1. The loss of dissolved value in the final cake is thus minimized.

Continuous countercurrent decantation, an adaptation of a well-known principle,[1] was attempted in cyaniding by Randall (South Dakota) in 1901 and by Denny (South Africa) in 1903, using cone-shaped agitators. It was made a practical success by the application of the Dorr thickener, a series of three to five of these being used, together with a number of agitators, the ore being usually crushed in solution.

After leaving the first thickener, the partly thickened pulp passes through the group of agitators, which may be in series or series parallel, and then through the remaining thickeners, and is discharged with or without filtration. By setting the last thickener highest, and the others in steps leading to it, the decanted solution flows back by gravity in the opposite direction to the solid, while the thickened pulp is transferred by diaphragm pumps. If on a level, the solution may be moved by air lifts. Excess solution from the first thickener is precipitated and returned to the second or third one from the end; cyanide is added to one of the agitators.

Points essential to success are solution of the maximum gold or silver before leaving the agitator system and efficiency of settling in succeeding thickeners, to at least 50 per cent solid if possible; in most cases, and always if the percentage of solid in effluents is under 50, the final discharge should be treated on a rotary filter to reduce soluble losses. Underflow solution is always slightly richer than overflow, owing to some dissolving and to diffusion of adsorbed or absorbed solution.

The flow sheet of United Eastern mill shows conditions prevailing with a pulp difficult to settle. Theory and practical applications are discussed by Eames,[2] Dorr and Dougan at Elko Prince,[3] and W. O. North at United Eastern.[4]

[1] The countercurrent principle allows the original ore to be treated with solution fairly rich in precious metal, but when partly exhausted, it must come in contact with poorer solutions, finishing either with wash water or with solution carrying only traces of value. The valuable content of the reagent should be as closely as possible proportioned to that extractable from the ore it meets.

An approach to this ideal is the conveying of crushed ore through a launder or horizontal pipe while a slow stream of cyanide solution travels in the opposite direction. Mere prolonged agitation, or the continuous passage of pulp through a series of agitators without a countercurrent, is entirely opposed to this principle, the solvent becoming enriched as the ore is impoverished.

In any continuous system the time an average particle remains in any thickener or agitator is found by dividing the weight of pulp passing hourly into the total weight of pulp contained in that unit. The arrangement (series or parallel) of any group of units does not, therefore, affect the average time occupied by the pulp in passing the group. Lengthening out the series of units decreases the probability of the rapid escape or short circuiting of any particle. (*Cf.* pp. 181 to 184, of the volume entitled "Principles and Processes.")

[2] *Trans. A.I.M.E.*, Vol. 57, p. 142.

[3] *Ibid.*, Vol. 60, p. 84.

[4] *Ibid.*, Vol. 68, p. 548.

Residues may be discharged by sluicing where water is plentiful, and in some cases carried off by convenient streams, but more commonly require to be settled in dams. In some localities substantial dams must be built of concrete or masonry, or heavy timber, but it is more usual to construct the dam from the coarser portion of the tailing itself. Sometimes empty cyanide boxes or drums are filled with sand to form the initial wall, or cells of light woodwork are similarly filled, or the tailing itself is shoveled up to form a retaining wall. The sluiced tailing is then roughly classified in such a way as to deposit the coarser material near the dam wall, while the finer settles nearer the middle, where a steeply inclined or vertical overflow box may be arranged, the overflow level being gradually raised by adding slats when necessary. Where possible, it is convenient to have two or three dams or sections, one of which may drain and consolidate while another is in use, the more solid portion being then shoveled up to form the wall. A fair proportion of clayey material, or of contained lime, makes an excellent binder for the heavy sand, so that such dams may be built up on suitable slopes to a great height.

Sand residue may be removed by shoveling through bottom doors or by a mechanical excavator, such as the Blaisdell, and carried off in cars, or by aerial conveyers, or by a conveyer belt which may deliver it to an elevating stacker. Slime, dewatered by a rotary or other filter, may be similarly carried off.

Or the tailing, sluiced or in cars, may be used for filling the stopes from which it originated; if more than a trace of cyanide remains, it may be necessary to decompose it by addition of permanganate.

Slime residues, thickened or settled without a filter, may usually be conveyed in pipes, but require a large area for satisfactory collection.

Watercourses below residue dams are liable to contamination sufficient to cause the death of birds and animals unless due precautions are taken. Whenever possible, it is desirable to pump any accumulated liquid back to the plant as a matter of precaution, as well as of economy on account of contained cyanide and precious metal.

"Dissolved values" carried to residue dams behave differently according to climatic conditions. In arid regions, evaporation takes place rapidly and salts effloresce at the surface, forming a thin layer of much enriched material—in some cases worth $100 per ton—which may be collected from time to time by careful sweeping or scraping, and returned to the plant. Where the rainfall is fairly heavy, the surface is usually impoverished; in some cases reprecipitation takes place on organic matter near the floor of the dam, in others some recovery may be made by precipitating the seepage by zinc boxes or, if acid, by scrap iron.

Similar dams may be used for the storage of untreated tailing intended for subsequent treatment. These should be constructed with a view to the reclamation of the tailing, removing trees and other obstructions, leveling the bottom, and excluding organic matter when possible; sand and slime may advantageously be segregated.

PRECIPITATION

Electrolysis as a mode of precipitation attracted many inventors as it seemed reasonable to expect a large measure of regeneration. Siemens & Halske used multiple iron anodes and thin sheet-lead cathodes, which were to be removed and cupeled after accumulating a suitable amount of gold; the current was of low voltage and a density of 0.04 to 0.06 amp. per sq. ft. The iron anodes were encased in hessian (burlap), but much Prussian blue and other by-products complicated the process, and the loss of iron was 0.3 to 0.5 lb. per ton treated. The main difficulty was the excessive electrode area and tank volume required approximately to exhaust a solution, the electrodes being 1 to 1.5 in. apart and 20 sq. ft. or more in area.

Butters modified the process by using tinned iron cathodes and much higher current density; Andreoli invented anodes of lead coated with lead peroxide; Cowper-Coles used anodes of peroxidized lead and cathodes of aluminum, from which the deposited metal was to be stripped in sheets.

Several inventors attempted to precipitate the gold as an amalgam by using as cathode a layer of mercury or an amalgamated copper plate. Some filtered the solution, others attempted to precipitate on plates suspended in the pulp during agitation; some added common salt to increase the conductivity, but in no case was entire success attained. Pelatan and Clerici introduced several apparatus for this purpose, and others were devised by Riecken, Hendryx, Oliver, Mumford, Hebaus, and Noriega.

Sodium and Sodium Amalgam.—The ideal precipitant for gold and silver from cyanide solutions would be metallic sodium, completely regenerating the alkaline cyanide:

$$Na + NaAu(CN)_2 = Au + 2NaCN$$

Attempts to use this reaction by means of sodium amalgam have not met with practical success. Molloy proposed to make metallic sodium by electrolysis of Na_2CO_3 solution with a mercury cathode communicating with and diffusing into a body of mercury kept in contact with the cyanide solution; others sprayed sodium amalgam through a rising stream of solution, or kept it moving by means of amalgamated disks.

Aluminum and zinc stand next to sodium in the line of available positive metals, and have proved the most practical precipitants for gold and silver. Each replaces silver in solution, but aluminum forms no double cyanide and requires the presence of some free alkali. The equation

$$Al + 3NaAg(CN)_2 + 3NaOH = 6NaCN + 3Ag + Al(OH)_3$$

indicates the complete regeneration of NaCN and the formation of alumina, which, however, dissolves in NaOH to form an aluminate, which may be assumed to be $NaAlO_2$. The $NaAlO_2$ reacts with CaO in solution to form insoluble $CaAl_2O_4$. Gold is not readily precipitated by aluminum, unless a fair proportion of silver is present; mercury is, precipitated but copper is not.

Aluminum dust has been successfully used in silver mills at Cobalt; it is fed in a manner similar to zinc dust, but must be retained in a special agitating tank to increase the time of contact. Hamilton's system, in use at Butters' Divisadero plant, involves the removal of calcium by a minimum of soda ash prior to adding aluminum, the aluminum passing into solution being later thrown out by lime used in the mill. Hamilton states that, in practice, 1 part of aluminum precipitates only 3 of silver in place of the calculated 12, the difference being mainly due to a reaction with NaOH to yield hydrogen. Alumina in the precipitate makes refining difficult.

With zinc, the essential reaction is, similarly, a replacement of gold and silver, the zinc going into solution as double cyanide:

$$Zn + 2NaAu(CN)_2 = Na_2Zn(CN)_4 + 2Au$$

No regeneration is apparent, but the double cyanide thus formed has a marked solvent action on gold and silver, which is increased by the presence of free alkali up to a ratio of about 4NaOH for each molecule, or about two and a half times the weight of zinc. Precipitation is complicated by side reactions, especially the evolution of hydrogen by reaction of Zn with NaCN and NaOH forming additional $Na_2Zn(CN)_4$ and Na_2ZnO_2 (zincate); this H further reacts to form sulphide by reduction of NaCNS and other sulphur salts, the Na_2S then precipitating Pb, Hg, or Ag as sulphide instead of metal. Some precipitation of Hg, Cu, etc., is due to direct action of zinc. Christy and others

have written equations purporting to show a definite proportion between Au and H produced, but there is no fixed relation.

Zinc shaving was recommended by MacArthur and Forrest for a "metallurgical filter" after testing various forms of zinc. U. S. patent 418138 (1889) describes a vessel or series of vessels, with perforated false bottoms, carrying a sponge of "filiform zinc" cut by turning tool from a series of zinc disks, solution being arranged to rise through each section of a set of boxes or compartments.

Zinc boxes are made of wood or steel, occasionally of cement, sometimes in units but usually in a series of five or six similar compartments, each with a false screen bottom, the new zinc being added at the lower end and moved up as it disappears from the upper end. Each section usually has a plugged bottom hole communicating with a pipe or enclosed launder which leads to a tank or receiver for use at the cleanup; the top is often covered with coarse screen as a precaution against theft. At a cleanup, the fine material is shaken down and washed through the screen bottom, and drawn off or washed down to the receiving tank, from which it is pumped to a small filter press. A considerable amount of precious metal is held back by the residual zinc moved to the head compartments. Some "short zinc" often has to be separately treated. It is advantageous to increase the space beneath the false bottom of the head compartments. The actual zinc-filled space usually recommended is 1 cu. ft. for each ton of solution daily precipitated, but in practice it may be one-quarter to double this. Five compartments are usually sufficient, but it is advisable to keep an empty compartment at the tail end.

Suitably packed, a cubic foot of fine zinc shaving weighs about 6 or 7 lb., but the coarser material used for silver may weigh 14 lb. It is now made by soldering together sheets of rolled zinc and coiling this closely on a roller or mandrel, which is then set in a lathe and cut by a chisel making an oblique cut at the ends. It is desirable when cutting to wind the thread into hanks of a size to fit the boxes in which it is used.

If the shaving is assumed to be a continuous rectangular strip of width a and thickness b in., the surface exposed by 1 lb. of zinc is

$$0.055\left(\frac{1}{a}+\frac{1}{b}\right) \text{ sq. ft., or nearly } \frac{0.055}{b} \text{ if thin}$$

If the section is not rectangular, but a parallelogram of angle A, this must be multiplied by cosec A.

Zinc dust as a practical gold precipitant was first used by Sulman at Deloro, Ontario, added intermittently to a rising stream of solution in an inverted cone, and passing to a filter. Later Waldstein and others added it by sprinkling it dry or as an emulsion in large charges upon vats of solution in a state of agitation, which was then pumped through square filter presses. Merrill introduced the practice of feeding it continuously to a moving stream of solution and using a triangular filter press; this system is now in use at nearly all the larger plants on the American continent, and is gradually displacing shavings elsewhere.

Feeders of several types are in use. One of the best is a slow-moving horizontal belt, on which a charge sufficient for several hours is spread in a uniform layer; this falls into a small mixing cone through which a trickle of auxiliary solution conveys it to the pump suction pipe. Another is a hopper at the outlet of which revolves a roller or pulley which removes a narrow ribbon of dust, the thickness of which is regulated by an adjustable slot. Or the zinc may be removed from the hopper by an augerlike horizontal screw. These feeders require a jarring mechanism to prevent the dust from adhering or bridging. Sometimes a miniature tube mill is added as a mixer. For accurate measurement it is convenient to have duplicate tanks of 100 or

200 tons capacity, which are precipitated alternately, but a large single tank may be pumped continuously while solution flows into it.

Abandoning air agitation effected a considerable saving of zinc, but the most marked improvement in precipitation has been the Crowe process of removing air from the solution by passing it through a vacuum tank on its way to the pump and just before introducing the zinc. Percolation through sand clarifiers containing some finely divided iron and pyrite has been recommended. In precipitating gold, the practical minimum of zinc dust is now between 0.1 and 0.05 lb. per fluid ton, or 25 to 50 parts of zinc per million of solution. When starting a press after a cleanup, it is advisable to add 50 per cent or more dust in excess of the normal charge; this is gradually diminished in successive charges until the regular amount is reached.

If zinc dust consists of equal spherical particles of diameter d in., 1 lb. exposes a surface of $0.165/d$ sq. ft., and contains $7.544/d^3$ particles. At an average diameter of 1/10,000 in., 1 lb. exposes 1650 sq. ft., and 0.1 lb. spread through a ton of solution gives some 13,600,000 particles to the cubic inch.

For complete reaction 1 unit weight of Zn precipitates 6.03 units Au, 3.30 Ag, or 1.93 Cu, but the efficiencies obtained in practice are often extremely low, sometimes only a fraction of 1 per cent with low-grade gold solutions; with rich silver solutions 50 per cent may be reached, if complete exhaustion of the solution is not aimed at. Gold solutions can usually be precipitated with zinc dust to within 1 cent per ton, with less expenditure of zinc than shavings require.

The best zinc dust was formerly imported; it usually contained about 2 per cent lead and often some cadmium; a much more efficient dust is now made in the United States, practically free from foreign metals and extremely uniform in size, the finer grades nearly all passing a 300-mesh sieve. It invariably contains oxide, often between 5 and 10 per cent ZnO. but this is not visible under a microscope, which shows uniform bright spherides. [illegible] and surface layer of 10 per cent ZnO on spheres would be less than one-fiftieth the diameter. Extreme fineness is advantageous with low-grade gold solutions, but not necessary with the higher metal concentrations obtained from silver ores.

With zinc dust, 1 sq. ft. net filter surface suffices for 1.5 tons (or 50 cu. ft.) solution per day, or 6 tons per hr. per 100 sq. ft.; with clear solutions a press may be run for long periods at double this rate. Colloidal suspended matter soon increases the pressure and reduces the pumping rate. For gold solutions 2-in. distance frames are suitable, 3- or 4-in. for silver. On opening a press most of the cake falls into the wheeled tray placed beneath; the remainder is easily removed by scrapers.

The practical efficiencies obtained with zinc dust, and the accumulations of zinc in solution, have averaged about the same as with shaving.

The dust process involves a more expensive installation than zinc shavings, but has the advantage of greater compactness and cleanliness, and involves less labor in maintenance and cleaning up as well as less risk of theft. The periodical cleanup is absolute, while a holdover of several thousand dollars' worth of precious metal commonly occurs with zinc shavings, and makes it impossible to compare the actual with what is often called the "theoretical" recovery. After a destructive fire, precipitate in a filter press has been found intact, while zinc boxes have entailed great difficulty in the attempts to recover their contents. At a gold plant a press occupying a floor space of 5 × 14 ft. can easily carry a month's accumulation of $40,000.

The comparative cost of the two systems at any time depends, of course, upon the wage scale and the relative prices of zinc dust and spelter. The Crowe process effects an economy in both.

Zinc in other forms has occasionally been used as a precipitant, such as small disks, slugs, or balls in a rotating cylinder or pan through which solution passed.

Sodium sulphide, Na_2S, does not appreciably affect gold or copper in cyanide solution, but precipitates silver as Ag_2S from $NaAg(CN)_2$, at the same time regenerating NaCN and carrying down some gold in the presence of a large proportion of silver. Owing to the reversibility of the reaction, either precipitation must be imperfect or a slight excess of Na_2S must remain in solution, which is an objection to its use, as is also the necessary further treatment of the precipitate. It was patented by Janin and Merrill in 1894, but was not used until adopted at Nipissing as a substitute for the expensive aluminum dust. The precipitate is here reduced to metal by the Denny process, by contact with slugs of aluminum in a tube mill.

Carbon as a Precipitant.—Graphite has no precipitant action whatever on gold or silver in cyanide solution, nor has wood fiber (cellulose). Charcoal, partly burned or charred wood, some varieties of decaying wood, and some of the carbonaceous material found in certain black or "graphitic" shales and slates, all precipitate gold from its solutions, some of them rapidly, and in some cases they may prevent its solution. Freshly burned charcoal is most energetic; after long storage it is much less effective, but the precipitating property may be largely restored by reburning. It is usually assumed to be due to occluded gases (CO or H), but nothing has been definitely determined on this point; these gases and the hydrocarbons in their ordinary form are quite inert. Coke and some varieties of coal have some precipitating effect, and in South Africa Caldecott patented the use of partly burned coal as a precipitant. In Australia, charcoal has been used to some extent as an actual precipitant, but the large volume required makes it inconvenient, and the final recovery of the gold is troublesome. Silver also is less completely precipitated.

The discovery, during the First World War, of means of activating charcoal, and the known high activity of coconut shell and other dense charcoals, and of kelp char, and the fact that fresh pine charcoal is almost equally effective as a gold precipitant, all suggest that charcoal has some practical possibilities if a better mode of application is discovered. Agitation with finely powdered, recently burned charcoal followed by filtration gives promising results on the small scale.

Edwards at Yuanmi, Western Australia, used three Butters-type vacuum filters in series, each of 260 sq. ft. surface and charged with 300 lb. of ground charcoal; this system precipitated 280 to 420 tons daily, leaving 7 to 8 cents gold in solution out of an original \$3.25. One filter was renewed every three days, making consumption 14 to 13 lb. per ton. The dried product was burned and the ash fluxed in crucibles with borax, sand, and salt.

Refining.—Dry cyanide precipitate may contain up to 70 per cent metallic zinc or ZnO; that obtained by zinc dust from gold ore averages about 25 to 40 per cent, that from rich silver ore much less. If precipitant and solutions were lead-free, precipitate from rich gold or silver solutions may be melted directly in crucibles with borax; it is more commonly acid-treated to remove zinc or sometimes roasted in iron muffles as a preliminary step. The removal of zinc by distillation in Faber du Faur furnaces has been used experimentally.

Borax is the most important flux, best used as crushed borax glass; the crystals contain 50 per cent of water. Soda ash and silica are also useful, depending on the impurities to be fluxed off; bicarbonate is sometimes used in place of soda ash, though more expensive and less efficient. Niter or sodium nitrate may be used to oxidize zinc, sulphides, etc.; manganese peroxide may be substituted, as it gives off oxygen more gradually; oxidizing agents attack graphite crucibles, and also tend to carry silver into the slag. Clay liners may be used to protect the crucibles. Fluorspar helps to maintain fluid slags. Litharge is used only when cupellation is the final step in the refining process.

Lead present in zinc or added to solutions appears in precipitate as metal or PbS, and sulphuric acid removes but little of it. Acid treatment, if followed by thorough washing, removes most of the zinc and calcium, and part of the copper. It is carried out in a lead-lined tank with a mechanical agitator, water being first introduced and strong acid added gradually to prevent boiling over. A suction fan is necessary to remove fumes, especially HCN, H_2S, and AsH_3; and care is also necessary on account of the hydrogen evolved. When action ceases, more water is added, the liquid is decanted on a filter or through a small filter press, the precipitate is then transferred to the filter and washed and finally dried to a stage where it can be handled without dusting. Sodium bisulphate, $NaHSO_4$, a by-product of acid works, may be used as a substitute for sulphuric acid.

After acid treatment silica, cadmium, mercury, and some copper remain with the precious metals, and some $CaSO_4$ and $ZnSO_4$; mercury may sometimes be profitably distilled off after adding lime or metallic iron to decompose HgS. On melting with reducing agents sulphates are deoxidized, yielding matte, which usually carries silver, as well as copper, lead, and iron.

Large crucibles, up to No. 400, may be used in tilting furnaces fired with oil, gas, or powdered coal; sizes 100 and smaller may be poured with hand tongs from wind furnaces using coke, etc. Electric heating has been but little used. In direct fluxing the cost of graphite crucibles is a serious item; melting may also be done without crucibles in tilting furnaces lined with carborundum or other refractory, or large crucibles may be set on a reverberatory hearth.

Rich silver precipitate is, at large plants, fused directly on a reverberatory hearth and tapped to molds; at Nipissing it is finished on the hearth by air-blast refining. United Comstock has an oil-fired tilting reverberatory.

The Tavener process, developed in South Africa, consists in mixing the precipitate with litharge and some sand, and smelting in a small reverberatory or pan furnace; the reduced rich lead is tapped off and cupeled.

At the Homestake, precipitate, raw or acid-treated, is partly dried and briquetted after mixing with a flux of borax, borax glass, litharge, and a little silica. The briquettes are fused in a small English cupel furnace on a test of Portland cement (three-fourths) and limestone (one-fourth) which is started by adding a little lead; the slag is tapped off from time to time together with some of the reduced lead. When all melted the surface is cleaned off and the lead cupeled on the same test, returning accumulated lead; the final slab of gold is broken up while still hot, melted in crucibles, and cast into bars. Low-grade precipitate is best briquetted, passed through a small blast furnace, and the lead cupeled.

The cupel slag, matte, and similar by-products are treated in a small blast furnace, and the lead is either cupeled directly or used to start cupellation in the next run. The litharge from the lead processes is ground and used for flux at the next cleanup.

If the precipitate is briquetted and treated raw, the increased losses in lead in slags, etc., offset any saving in acid. The holdover in blast-furnace by-product lead and litharge is less than 1 per cent of a month's run, and the only by-product to be marketed is the impoverished matte from the blast furnace.

In fluxing, 100 lb. of raw gold precipitate may give up to 100 or even 200 lb. of slag; after acid treatment and lead refining, about the same total of slag and litharge together, but the proportions vary greatly with the flux and condition of the precipitate.

At all plants large enough to justify the expense—treating, say, at least 400 or 500 tons daily—a small lead blast furnace is an excellent investment. Not only can the by-products of cyanide cleanups—and if necessary the entire cleanup after briquetting it or setting it with some binder—be treated economically in such a fur-

nace, but all sorts of by-products can be handled at intervals with little or no previous preparation, such as mill skimmings, rich pyrite, black sand, iron superficially amalgamated, old copper plates, sweepings, rich slags, and crucible scrapings. An important essential is to avoid charging finely divided material, or the blast may become choked and the furnace freeze. Fines must be briquetted or set with some suitable binder, such as water glass or acid.

In preparing cyanide precipitate for refining by means of a cupel or blast furnace, the expense is about the same whether a preliminary acid treatment is used or not; the use of acid effects an important reduction of the lead losses. If much zinc remains in the mass smelted, the slags become stiff from the presence of spinellike compounds, and more lead must be left in the slag. If the washing of acid-treated precipitate is imperfect, sulphuric acid or sulphate of calcium or zinc remaining, the SO_4 becomes reduced in the cupel or furnace and matte is formed.

In many cases the mixture of by-products is almost self-fluxing, requiring only the addition of a little limestone or assay slag to run freely. Fluorspar is sometimes useful in maintaining a fluid slag. In the final furnace by-products, such as matte, slag, and litharge, the ratio of silver to gold is generally much higher than in the bullion bars.

Air and Oxygen in Cyaniding.—The oxygen necessary to dissolve gold is supplied by air dissolved in the solution, which is slightly less than that carried by an equal volume of water. Additional oxygen may be furnished in leaching by allowing the solution to drain low before adding more, and thus entraining air; sometimes air is blown for several hours at a time through the filter bottom after draining a charge, and it may be similarly blown through charges of slime in the filter press.

In slime treatment, air thus serves a double purpose, being used as a mechanical agent in agitation or air lifting, as well as to aid solution of gold; when transferring pulp by centrifugal pumps, air is sometimes admitted at suitable openings, and one of the advantages of the "double treatment" of sand is to admit air freely.

The oxygen required for actual dissolving of gold is small in quantity. Assuming the interstitial space in sand as 50 per cent, the solution contained in a ton of saturated sand (specific gravity, 2.6) would suffice to dissolve over 2½ oz. of gold or 1.5 oz. of metallic silver, were it not used up by reducing agents, but to oxidize these reducing agents (mainly ferrous and sulphur compounds in ore, or organic matter introduced) a large volume of additional air must be supplied. In precipitation, the presence of O is undesirable; see under Crowe Process (page 328). Deep agitators and pressure filtration favor the dissolving of O, while vacuum treatment removes it from solution.

Excessive use of air is undesirable, as it carries off some HCN due to hydrolysis of NaCN, but free alkali almost entirely prevents this. The CO_2 in atmospheric air also tends to decompose NaCN; the CO_2 in 1000 cu. ft. of free air at sea level will decompose about 0.1 lb. NaCN, or consume 0.06 lb. of CaO, yielding over 0.1 lb. of $CaCO_3$. It may be removed by washing the air with caustic soda or lime water. Accumulation of $CaCO_3$ on cloth gradually reduces its permeability; this is partially restored by treatment with dilute HCl, but each successive acid wash leaves the cloth a trifle less effective than the preceding. Air from compressors usually carries oil, which produces an objectionable coating on filter press cloths; this oil may be excluded by passing the air through a special filter press of a few large frames.

At sea level and freezing point, 1000 cu. ft. of dry air contains 18.65 lb., 8.6 kg., or 272 troy oz. of oxygen. But at ordinary ranges of temperature and atmospheric moisture, the O actually present is between 90 and 95 per cent of these weights; at higher altitudes, the weight of O per 1000 cu. ft. is directly proportional to the lower barometric pressure. It is convenient to read this by a mercurial barometer and to note that the pressure of a 1-in. column = 0.49 lb. per sq. in., also that the barometer falls about an inch for each 1000 ft. elevation from the normal 30 in. at sea level.

Barometer, inches mercury..........	30	25.0	20.0
Approximate elevation corresponding	0	5,000 ft.	10,000 ft.
Pounds per square inch.............	14.7	12.25	9.80
Relative solubility of oxygen........	100	83.3	66.7

Solubility of Oxygen in Distilled Water When Exposed to Air at Sea Level (Winkler)

Temperature, Centigrade...............	0	5	10	15	20	25	30
Temperature, Fahrenheit................	32	41	50	59	68	77	86
Oxygen, cubic centimeters per liter[1].....	10.2	8.9	7.9	7.0	6.4	5.8	5.2
Oxygen, milligrams per liter[2]...........	14.6	12.7	11.3	10.0	9.15	6.15	7.6

[1] From an atmosphere of pure oxygen the solubility is about 4.8 times this. Nitrogen from air dissolves at approximately double these volumes.

[2] Multiply these weights by 0.002 for pounds O, and by 0.029 for troy ounces O, per ton of water.

For cyanide solutions, at sea level, it is safe to assume the solubility of O as over 90 per cent of that in water (Maclaurin found 87 per cent for 1 per cent KCN, 50 per cent for 10 per cent KCN) and at higher altitudes, to reduce this proportionately to barometric pressure. Thus at 5000-ft. elevation the maximum solubility of O in ordinary solutions may be taken as about 8 mg. per l., or 8 parts per million, which is about 0.23 troy oz. per ton, sufficient to dissolve 5.7 oz. gold or 3.1 oz. metallic silver.

In working with deep tanks, and especially at high altitudes, it is important to remember that the solubility of oxygen varies with the absolute pressure (gauge + atmosphere). In a slime tank containing pulp of specific gravity P, at a depth of H ft. from the surface, the gauge pressure (pounds above atmosphere) $= 0.433PH$. Thus in a Pachuca tank, 45 ft. deep, filled with pulp of specific gravity 1.2, the pressure at bottom $= 0.433 \times 45 \times 1.2 = 23.4$ lb. per sq. in.

If this is at an elevation of 5000 ft., with barometer standing at 25 in. ($25 \times 0.49 = 12.25$ lb.), the solubility of oxygen at the bottom will be nearly treble that at the surface.

$$\frac{23.4 + 12.25}{12.25} \quad 2.91$$

In working with thick slime the *rate of solution* of oxygen, like that of other substances such as gold or cyanide, is much diminished as compared with thin pulp or clear solution.

Solutions recently precipitated with zinc or aluminum, especially after vacuum treatment, are practically free from oxygen and nearly saturated with hydrogen and, therefore, in the most unfavorable condition for dissolving gold; they should be given an opportunity to aerate by cascading, spraying, or agitation.

Heating Solutions.—Both the dissolution and precipitation of precious metal, as well as the settling of slime, are accelerated by a moderate rise in temperature, and systematic heating of solutions has often been proposed. It has been advantageously carried out with extremely cold solutions, or to assist in thawing frozen ore. Heating above 50 or 60°F. is, however, of doubtful value, as it diminishes the solubility of oxygen and favors decomposition of cyanide.

When exhaust or cheap steam is available, it may be led through coils or zigzag pipes near the bottom of solution tanks or sumps; conveying pipes and launders should also be protected from cold.

The settling of slime and filtering of solution through sand are also facilitated by heating; the rate of settling (and, therefore, the capacity of settling tanks, etc.) is inversely proportionate to viscosity of liquid. The settling rate of a slime is proportional to $T + 10$, where T = temperature Fahrenheit. Thus if a particular slime settles 18 in. per hr. at 40°F., its settling rate at 60° will be $\frac{60 + 10}{40 + 10} \times 18 = 25.2$ in. per hour. The same rule holds approximately for filtration rates.

In crushing ore, most of the energy applied to the machines becomes available as heat in the resulting pulp. As the specific heat of most ore and rock is between 0.2 and 0.25, that of solution being practically 1, it is easy to compute roughly the rise of temperature that may be expected. With low water ratios it is often of importance as an insurance against freezing. One hp.-hr. = about 2550 B.t.u. and raises a ton of water about 1.25°F., or a ton of dry ore 5 to 6°F.

Fouling of Solutions.—In the earlier days of cyaniding much was said of the fouling of solutions, and it was necessary at times to dispose of "fouled" solution and make a fresh start. This is now rarely necessary; solutions are used continuously for many years without renewal and without material change in composition. The daily elimination of solution in residues, and in first and last drainings, is an appreciable percentage of the whole stock of plant solution, so that the solution is practically renewed every few months.[1] Zinc is removed to some extent by precipitation or adsorption on the ore or tailing.

Regeneration of the cyanide usually lost as a solvent has proved an attractive field for invention, but so far has met with comparatively little success. The following lines have naturally suggested themselves.

1. Precipitation of precious metal by a metal simultaneously regenerating NaCN, such as Na directly, or Al indirectly; Zn itself has some effect, as its double cyanide is a feeble solvent, rendered more active by the presence of free alkali. Electrolytic precipitation may be included here.

2. Oxidation of HCNS to HCN + SO_3 or of NaCNS to yield NaCN + SO_3, the latter with alkali forming sulphate. This may be effected by electrolysis or by certain oxidizing agents, but the yield has always been disappointing, owing to decomposition of the product. In this connection, reference must be made to the Clancy project.

3. Neutralization or acidification of solutions; on the one hand, yielding insoluble cyanides [CuCN, AgCN, $Zn(CN)_2$; CuCNS, AgCNS; occasionally ferrocyanides], and on the other, liberating HCN. The precipitates must be separated to recover Au, Ag, and part of their contained CN by suitable means; the HCN may be removed at least partially from the solution by heat, by passing a current of air or gas, or by applying a vacuum as in the Crowe process. Gaseous HCN thus liberated may be absorbed in a suitable alkaline solution to form NaCN or $Ca(CN)_2$, or the HCN in solution may be fixed by addition of alkali.

The general idea has been to operate upon "fouled solutions" or on the "low solution" normally and unavoidably thrown away daily in some form. The low

[1] If p is the percentage of stock solution discharged daily, and x the percentage of any substance now present remaining in the system after n days,

$$\log x = n \log \left(1 - \frac{p}{100}\right) + 2$$

Thus, supposing 5 per cent of the stock is daily removed, only about 21.51 per cent of any material now in solution will remain after 30 days, 4.6 per cent after 60 days, less than 1 per cent after 90 days, etc. Hence, if any radical change is made in the treatment, such as substituting NaCN for KCN, the solutions soon reach practical equilibrium.

concentration of solutions in general use has militated against the completeness of precipitation and volatilization.

Filter Cloth.—Many varieties of filter cloth have been used in cyaniding ore, precipitation with zinc dust, and handling acid-treatment liquors. Cotton cloths of all the three common weaves—plain canvas with single or double thread, twill, and sateen—have been found satisfactory when the weight of material selected is suitable for the pressure and conditions of use. The more complicated weave known as chain cloth seems to have no sufficient superiority to justify its price. Paper is not generally to be recommended.

For precipitation it is convenient to use one of two systems: (1) a fairly heavy cloth backing, covered with light "domestic" or twill, the latter to be removed at each cleanup and burned, or washed and re-used once or twice; or (2) two layers of a medium-weight material, the outer to be removed at cleanup and either burned or washed for re-use. When re-clothing, a new or washed cloth is put next the plate and the original under cloth replaced above it. Occasionally three or four thicknesses of very light material have been used, the outer layer being taken off at cleanup and a new one placed next the plate.

For filter bottoms of leaching vats a heavy canvas (such as No. 8 or 10-oz. duck) is desirable and will last one to two years. It may be acid-treated in place if the usual accumulation of calcium carbonate checks the leaching rate decidedly. A similar cloth may be used in filters of the Moore and Butters types; for slime presses a similar heavy canvas may be covered with a light or medium twill. These may similarly be acid-treated by using hydrochloric acid, so highly diluted as to avoid attacking the iron frames.

The nominal "ounces" rating of canvas refers to the weight of a running yard of a standard width of 22 in.; the "ounces" may be read directly by noting the weight in grams of a sample cut 4 × 7 in. (28 sq. in., or 180 sq. cm.). The "number" is approximately obtained by subtracting the "ounces" from 19. Thus if a sample of duck, 4 × 7 in., weighs 9 g., it indicates "9-oz." duck, or "No. 10." Figures thus determined usually agree within one unit with the commercial ratings, but dealers occasionally apply the ounce rating to the square yard, making the nominal weight about 60 per cent too high. The present tendency is to specify weight per square yard, irrespective of the actual width of fabric.

MODIFICATIONS OF THE CYANIDE PROCESS

Bromocyanide Process.—This depends on the reaction

$$BrCN + 3NaCN + 2Au = 2NaAu(CN)_2 + NaBr$$

the BrCN being added as such, or obtained from bromide and bromate:

$$2NaBr + NaBrO_3 + 3NaCN + 3H_2SO_4 = 3BrCN + 3Na_2SO_4 + 3H_2O$$

The bromocyanide process has been used in Western Australia, and to a limited extent in Canada and Colorado. An excellent résumé with bibliography is given by Stevens and Blackett.[1] Bromocyanide can be used to advantage only on two classes of ore: (1) ores containing minerals such as tellurides, more soluble with this reagent than with plain cyanide; (2) ores requiring rapid dissolution of gold in order that other substances in the ore shall not have time to dissolve and foul the solution. A preliminary treatment with plain cyanide is always advisable. No appreciable amount of free alkali must be present. BrCN itself decomposes rather rapidly in solution and also induces wastage of NaCN. BrCN is rather

[1] *Trans. I.M.M.*, Vol. 29, p. 280.

expensive, and so are the mixtures from which it may be prepared (Br + NaOH + NaCN, or NaBr + $NaBrO_3$ + NaCN), and the "mixed salts" used for this purpose are liable to decomposition in storage. Cyanogen chloride cannot be substituted, and ICN is too expensive.

Gitsham Process.—Free HCN in the presence of oxygen has a slight solvent action on gold. This process proposes to use feebly acid solutions, especially for ores containing antimony, copper, and other base metals. The effluent solutions are to be neutralized by lime before precipitation by zinc, and reacidified with addition of enough alkaline cyanide to bring them up to suitable strength.

Gilmour-Young Process.—This system was devised at a Nicaragua mine to utilize the existing Boss process pans for cyaniding rich ore. Copper amalgam was made by treating mercury with copper sulphate and iron filings, the squeezed product carrying about 15 per cent copper; zinc amalgam was sometimes added. A charge of dry ore was ground with cyanide solution and about 200 lb. of mercury for 2 hr.; 30 lb. of copper amalgam was then added, and the whole ground 4 hr. longer, when the mercury was separated. The squeezed amalgam was enriched by repeated use and finally retorted, yielding bullion 700 to 750 fine.

Diehl and Marriner Processes.—These were evolved to treat the rich telluride ores of Western Australia. The Diehl process consists in wet crushing, sliming, and treatment first with KCN and then with BrCN in agitation vats and filter presses. The Marriner system involves dry crushing, roasting, amalgamation, and treatment of the roasted ore by percolation or by fine grinding and filter press. There were many modifications of each system in use; the results and costs did not differ greatly, as the cost of bromocyanide in one case offset that of roasting in the other. With the wet process, concentration was often practiced, and the concentrate roasted preparatory to cyaniding.

The Usher process was an African slime method in which, after one stage of agitation, solution was introduced by multiple pipes over the bottom of a flat or cone-bottomed tank, and the upper clear portion continuously decanted for precipitation. Finally the slime was allowed to settle as usual. In one modification of the process umber, containing manganese peroxide, was used as an oxidizer.

The Denny desulphurizing process is used at the Nipissing Mine, Cobalt, to prepare silver sulphide ores for cyanidation. By grinding them in tube mills with ingots or slugs of aluminum and caustic soda, all silver minerals are decomposed, except dyscrasite, yielding metallic silver which is amenable to cyanide. At the same time Na_2S is formed, which can be used as a precipitant. The process is completed by agitating the pulp 12 hr. in a tank lined with aluminum plates.

Antidotes to Cyanide Poisoning.—The following materials should be kept at every cyanide plant and laboratory; sets should be placed at convenient points on every floor at which solutions are handled.

One sealed bottle (preferably a quick-opening "citrate of magnesia" bottle with rubber gasket), containing 1.5 g. of caustic soda, NaOH, dissolved in 300 cc. of water.

One sealed bottle (preferably a 2-oz. wide-mouthed bottle with large projecting cork), containing 7.5 g. (¼ oz.) of ferrous sulphate crystals dissolved in 30 cc. (1 oz.) of water. This water should be freshly boiled, and the vacant space in the bottle filled with carbon dioxide or hydrogen, to prevent oxidation; the cork must be completely covered with melted paraffin or sealing wax.

One corked tube containing 2 g. of finely powdered magnesia.

A large cup, of at least a pint capacity, preferably of white enamelware, which will hold the three previous items, together with a spoon or flat stick for stirring them. When required, the ferrous sulphate is to be poured into the cup, followed by the soda and magnesia, and the whole well stirred and swallowed; no time should be wasted.

It is desirable to add a rubber stomach tube and a wooden gag, so that the antidote may be poured into the stomach of an unconscious patient if necessary.

These materials should be kept in a glass-fronted cupboard, easily accessible and conspicuously marked, and all foremen and shift bosses fully instructed in their use. The soda requires renewal after 2 or 3 years, as it slowly attacks glass. The ferrous sulphate also oxidizes slowly, but a small amount of yellow deposit may be ignored, as long as the solution remains strongly green.

The above is known as the Martin antidote, and was developed by Dr. C. J. Martin and R. A. O'Brien, of Melbourne, in 1902. Variations of the outfit have been put on the market by different dealers, but the equipment can be easily prepared at any laboratory. The essential reaction is the formation of ferrous hydroxide, avoiding any excess of caustic soda, and conversion of the cyanide into harmless ferrocyanide.

Among other remedies that have been suggested are: hydrogen peroxide (2 per cent solution used hypodermically and as a stomach wash), cobalt salts, adrenalin, sodium cacodylate, and silver nitrate (dilute solution followed by an emetic of salt water and mustard).

Plant Precautions.—An eczematous condition of the skin may be caused by long contact with strong cyanide solutions. This should be avoided at cleanups of zinc boxes by greasing the hands and wearing rubber gloves in handling wet shavings; it is unnecessary to handle solution at other times.

Zinc shaving and dust, and aluminum dust, are decidedly inflammable. Caustic soda falling on zinc dust reacts with the evolution of enough heat to ignite the liberated hydrogen and cause the zinc to smoulder. Extinguishers of the carbon tetrachloride type must not be used on zinc-dust fires, as the reaction ($Zn + CCl_4$) yields various toxic and irritating gases.

MINOR AND OBSOLETE PROCESSES

Chlorination Process for Gold.—This process was based on the fact that chlorine, in the presence of moisture, converts gold into the trichloride ($AuCl_3$), which is soluble in water and removed by washing; the gold being then precipitated by ferrous sulphate, sulphur dioxide, hydrogen sulphide, or charcoal. Coarse gold requires long contact and should be removed by amalgamation. Pyritic ore or concentrate requires a dead roast before chlorination; thoroughly oxidized ore may be treated directly. Basic ores—containing lime and especially magnesia—absorbed much chlorine and might become heated. This was checked by roasting with a high temperature at the finish, to frit the magnesia with silica. Chlorination was suggested by Percy and by Plattner independently in 1848, though Plattner apparently made the first commercial application of the process to the arsenical ores of Reichenstein, Silesia.

The *Deetken* or *California* process was carried out in comparatively small wooden vats with bottom filter of perforated boards, resting on slats and covered with coarse gravel and sand; a vat 8 ft. in diameter with 3-ft. staves would hold about 3 tons. The crushed and roasted ore was loosely charged by sifting in a moist condition to facilitate leaching, a cover was luted on with clay or dough, and gaseous chlorine generated in a lead vessel from manganese dioxide, salt, and sulphuric acid was admitted by a lead pipe to the bottom until it could be detected at a hole in the cover. In later practice, liquid chlorine was purchased in steel cylinders. After 12 to 36 hr. contact (adding more chlorine if necessary), water was turned in at the top, any chlorine escaping at the bottom pipe being led to another vat. The yellow solution was run to the precipitating vat and the charge washed until the effluent was colorless. The residue was then shoveled out; if much silver was present it was transferred to another vat

and leached there with hyposulphite solution. Some ores, rich in silver, were first leached with hyposulphite and then chlorinated.

The *barrel* process, used on a large scale in Colorado, involved the rotation of the ore in barrels of wood or heavy lead-lined steel, holding 5 to 25 tons, while chlorine was generated under pressure in the mass by means of bleaching powder and sulphuric acid. Barrels were often built with an internal filter on one side, consisting of pebbles or coarse sand confined by slotted boards and a perforated lead plate. After 3 to 6 hr. water under 20 to 40 lb. pressure was admitted by a trunnion and washed the charge in 1 to 2 hr. A ton of ore would use at least 10 lb. of bleach and 15 lb. of sulphuric acid. The ore was charged dry from a hopper and discharged by sluicing through manholes in the side.

The *Munktell* process consists in leaching the ore with two solutions, one of bleaching powder, the other sulphuric acid, which mix at the time they are applied. At Mt. Morgan, Queensland, a solution of chlorine in water was similarly used, 100-ton charges of ore being leached in rectangular concrete vats, $60 \times 12 \times 5$ ft., lined with pitch and provided with bottom filters of sand resting on perforated planks and joists. This was superseded by the permanganate-chlorine process.

The *Black-Etard*, or permanganate, process employs long contact with a solution of potassium permanganate, salt, and sulphuric acid (about 6 lb., 120 lb., and 140 lb. to 5 tons or 1000 imp. gal. of water), the color indicating its strength. The original Etard formula used permanganate and hydrochloric acid.

The *Mears* process is barrel chlorination in which gaseous chlorine is pumped into the charge under its own pressure. Thies first employed bleaching powder and acid to produce the pressure. Newbery and Vautin used air pressure to accelerate the action of the chlorine, and the Pollok patents specify water pressure. Ankeny used the more expensive bromine in place of, or in conjunction with, chlorine. Many other early patents dealing with chlorine and bromine are described in O'Driscoll's "Notes on the Treatment of Gold Ores."

In California, precipitation was usually effected by ferrous sulphate, made by the action of sulphuric acid on scrap iron. Sulphur dioxide was commonly used in conjunction with the Colorado barrel process, generated in iron retorts from sulphuric acid and sulphur or charcoal, or hydrogen sulphide, and sawdust filters. Charcoal was used as precipitant at Mt. Morgan. The solutions were usually passed through boxes filled with scrap iron to precipitate copper or silver before being discharged.

Roasting was usually effected in California by hand-rabbled wood-fired reverberatories; elsewhere in White-Howell or Bruckner cylinders, Pierce turret furnaces, Merton or Edwards furnaces, etc. At Mt. Morgan the Richards furnace was used, cascading the ore from successive shelves. Residues from pyritic ores were often ground for paint.

The Patera process utilizes the solubility of silver chloride in solution of sodium thiosulphate, $Na_2S_2O_3.5H_2O$ (the hyposulphite of photography) and precipitation of silver as Ag_2S by Na_2S. This was suggested by Percy and first applied by von Patera at Joachimsthal in 1858.

The ore is roasted with addition of salt (4 to 8 per cent), part of it being added near the finish; the hot ore is wetted and allowed to stand some hours to favor chloridizing of the silver. It is then bleached in wood vats with warm water to remove base-metal chlorides which also dissolve a little AgCl. Hyposulphite solution is then applied and finally wash water, and the effluent run to "base metal" tanks until a trace of hypo is found, then to the silver tanks. The base solution may be precipitated by Na_2S, or Ag may be thrown down by cement copper, and copper by scrap iron, or iron may be used at once. The silver solution is precipitated by sodium

sulphide, carefully avoiding an excess; after separating Ag_2S by settling or filtration, the solution can be used again.

A suitable solvent is 0.5 per cent of crystallized $Na_2S_2O_3.5H_2O$, but up to 2 per cent may be used in absence of base metals; 1 ton of 0.5 per cent solution dissolves 30 to 40 oz. of silver. It also dissolves $PbSO_4$ and $PbCl_2$; adding Na_2CO_3 then precipitates $PbCO_3$. Sulphates retard solution of silver; free alkali is more prejudicial.

Commercial sodium monosulphide may be used as precipitant, or a polysulphide (Na_2S_4 or Na_2S_5) may be made by heating caustic soda with sulphur (see under Kiss Process).

The vats used were generally small, occasionally up to 25 or 50 tons capacity. The precipitated sulphide was usually filtered in conical canvas bags hung on iron rings in a frame; a filter press was sometimes used. The dried precipitate was sometimes refined by charging upon fused lead on a cupel, or might be smelted with lead ores.

The Kiss process nominally substitutes calcium thiosulphate and sulphide for the sodium salts used by von Patera. The precipitant is usually made by boiling lime and sulphur by means of steam, yielding polysulphide and thiosulphate:

$$3CaO + 12S = 2CaS_5 + CaS_2O_3$$

The precipitated Ag_2S is therefore mixed with excess sulphur, and thiosulphate is added to the solution. Starting originally with $Na_2S_2O_3$ this would gradually be replaced by the calcium salt, but part of the calcium is usually precipitated by sulphates as $CaSO_4$, and additional sodium is introduced from salt in the charges. About 3 lb. of lime and 2 lb. of sulphur with a ton of water would make enough precipitant for 50 to 100 lb. of silver.

O. Hofmann states that, with ores containing little or no Cu, the percentage of silver chloridized may be increased by using $CuCl_2$ (or a mixture of 3 to 4 lb. bluestone and 6 to 8 lb. salt per ton of ore), added by degrees to the preliminary wash water.

In the Russell process, it is claimed that a treatment with "extra solution" containing some $Cu_2S_2O_3$ (prepared by adding bluestone to thiosulphate) extracted additional silver and was much more effective in dissolving gold.

The Augustin process consisted in giving a chloridizing roast to silver ore or matte, and leaching with a strong solution of common salt, which dissolves silver chloride to a limited extent. The silver was then precipitated by metallic copper, and the copper by scrap iron. The cement copper was then melted and granulated for re-use.

The Ziervogel Process.—Argentiferous matte was roasted to form sulphates, cautiously raising the temperature to decompose those of iron, copper, etc., while silver sulphate remained unchanged, and was leached out by hot water. The process was also applicable to ore.

Silver sulphate (Hofman and Wanjukoff) begins to decompose at 917°C. and is completely reduced to metal at 923; copper sulphate, stable up to 653, is completely converted into CuO at 736°; zinc sulphate at 767; ferrous sulphate passes into basic ferric sulphate between 167 and 480°, while ferric sulphate begins to dissociate at 492 and is completely converted into Fe_2O_3 at 560°C. Ag_2SO_4 dissolves in 180 parts of cold or 90 of hot water, and is much more soluble in hot dilute sulphuric acid; in either case it is precipitable by copper, iron, or sulphides.

In the Claudet process, the product of a chloridizing roast of copper pyrites was leached with solution of sodium and ferric chlorides, which dissolved AgCl, $CuCl_2$, and some $PbCl_2$. By addition of ZnI_2 (or NaI) silver was thrown down quantitatively as AgI, together with some CuI and PbI_2 and any gold that may have dissolved. The precipitate was separated, washed, and reduced with metallic zinc, yielding spongy silver and a solution of ZnI_2, which was used again as precipitant.

Or, by digesting the precipitate of AgI, etc., with sodium sulphide, Ag_2S was formed and NaI regenerated as a precipitant.

Gibb's process was similar, but employed H_2S gas as a precipitant, until about 5 per cent of the Cu was precipitated, which ensured all the silver being thrown down.

SILVER AMALGAMATION

The Patio process was originated by Bartolomé de Medina about 1557, for the rich silver ores of Pachuca, and was widely used in Mexico and in South American countries. This process is described at length in Chap. XVII, Chlorine in Metallurgy.

The Patio process was worked for some time in Nevada on Comstock ore, but failed owing to climatic conditions, and this led to the adoption of the Washoe or pan-amalgamation process.

The Washoe process, or pan amalgamation, was developed at the Comstock mines, Washoe County, Nevada, the ore being stamped dry or wet, and the pulp treated in batches, usually three per pan daily. The pans differed greatly in detail, having cast-iron bottoms with wood staves or sheet-iron sides, and a central cast cone through which ran a vertical shaft carrying a muller with cast segmental shoes; similar cast-iron dies were attached to the bottom. Means for raising and lowering the muller were provided by threaded handwheels forming lock nuts at the top of the shaft, or by carrying the step bearing of the shaft on an adjustable lever. Three curved iron wings were usually fastened to the sides or hung from the wooden cover. A steam chamber was often provided under the pan bottom.

The charge was usually 1500 to 3000 lb., but might range from 800 to 5000. A batch of pulp was run in, after thickening in a wooden tank if wet-crushed; the muller was lowered and the charge ground 1 to 3 hr., steam being admitted to the false bottom, or run directly into the pulp by a hose. Mercury was then added, at least 10 per cent the weight of the dry pulp (often 300 or 350 lb. altogether), the muller raised clear of the dies and run 3 or 4 hr. Chemicals were generally added with the mercury, usually copper sulphate and salt, sometimes sulphuric acid or metallic iron, though the iron was often derived from the wear of the pan castings.

The pulp was then thinned with water and run to a shallow separator or settler with vertical shaft carrying four arms with iron or wooden plows. Here the bulk of amalgam and mercury separated and were drawn off at a siphon tap. In some cases this stage was carried out in the grinding pan, revolving the muller slowly.

The pulp then ran to an agitator--a deeper pan with wood sides, with four revolving arms carrying vertical slats—to settle a little additional amalgam and coarse material, and was finally drawn off, running to waste or to a settling dam. All settlers, etc., were provided with holes in the sides closed by wood plugs for discharging pulp. At the Comstock, 70 to 85 per cent is said to have been extracted from the sulphide ore, but at custom mills the usual return was only 65 per cent of the assay value of samples taken at the mortar lip.

Barrel amalgamation (Freiberg process) was carried out in stout wooden barrels rotating on a horizontal axis. The ore was roasted with salt and charged in the barrel with water and scrap iron, which dissolved silver chloride and reduced it to metal, cupric and ferric salts being also reduced to cuprous and ferrous; mercury was then added and rotation continued 16 to 20 hr., more water was then added to thin the pulp, and after a short period of rotation the mercury was drawn off and the ore washed out by a stream of water. This process was used for some time on the Comstock lode.

The cazo process or hot pan amalgamation was devised by Alonzo Barba in Peru about 1609 for rich oxidized silver ore. The *cazo,* or pan, first used was a small copper

pan; the later *fondon* had a copper bottom about 6 ft. in diameter and 6 to 8 in. thick, to which wood staves were fitted. Two large copper mullers were made to revolve around it, and a fire was maintained under the bottom. See pages 525 and 526 for a complete description.

The Boss continuous process was an attempt to make the Washoe pan-amalgamation process continuous, by using a series of steam-jacketed pans set on a slight grade so that pulp flowed from one to the other and finally through settlers; the mercury similarly flowed through a pipe system to a safe (as was done at some of the Washoe plants) where it passed through a conical canvas filter to separate solid amalgam, the filtered mercury being pumped back to the topmost pan.

The Reese River process, applied by Stetefeldt to the very base sulpharsenical ores of central Nevada, involved a chloridizing roast of the ore, wetting and cooling it on a floor, followed by a pan treatment similar to the Washoe process. A very impure bullion resulted. A similar system was used in Butte and elsewhere in Montana.

The Combination process, adopted by the Montana Co. about 1890, consisted in concentrating the gold-silver ore coming from the stamp mill before thickening the tailing and treating it by the pan process. A great economy in mercury was effected by thus removing arsenical copper minerals. The original equipment was 50 stamps with amalgamating plates, 20 frues, 24 pans, 12 settlers, 5 agitators, and finally 20 frues for the pan tailing, which was then impounded.

The Kroehnke process consisted in treating crushed ore in rotating wooden barrels of the Freiberg type, with mercury and a strong solution of cuprous chloride in brine, and then adding zinc amalgam; lead amalgam was used with poorer ore. The impure coppery amalgam was then purified by treatment with hot brine and bluestone acidified with sulphuric acid, and finally centrifuged and retorted. The process is thoroughly described by Schnäbel.

Conversion Tables for Assay Valuations.—In English-speaking countries the weights of precious metals are usually expressed in troy ounces (of 480 gr.) and fractions of ounces are stated in decimals, the troy pound, pennyweight, etc., being but little used. Other nations generally use the metric system for these as for other metals, and this system is adopted in many United States statistical reports. The purity or "fineness" of these metals is expressed either in carats (twenty-fourths) or in parts per thousand (millièmes), pure gold being designated as 24 k. or 1000 fine.

Gold.—The exact value of 1 troy oz. of pure gold was $20.671834625323+, corresponding to the coinage of $8000 from 387 oz. of fine gold, or 430 oz. of gold 900 fine, as the United States standard from 1834 to 1934. It is now $35.00 per ounce. Standard British coinage gold is 22 k. or 916.666 fine, and the price of gold in London is 168 shillings per ounce.

Silver.—In the United States the price of silver is stated in cents per troy ounce of metal nominally 1000 fine. London quotations are pence per troy ounce of "sterling silver" 925 fine, which, except for short periods, was the standard for British silver coin from 1066 to 1920. Since 1920, British silver coins have been reduced to a fineness of 500.

1 penny per ounce 925 fine = 2.19 cents per fine ounce.
1 cent per fine ounce = 0.457 pence per ounce 925 fine.

United States silver coin is 900 fine, 110 standard oz. or 99 fine oz., coining $128; the Mints report the fineness of silver bullion to the nearest one-half part per 1000.

The following foreign or obsolete units sometimes occur in reports: South America: 1 marco per cajon varies between 100 and 70 parts per million, or grams per metric ton. Russia: 1 dola ($\frac{1}{96}$ zolotnik) per 100 poods = 2.71 parts per million.

Fineness of Bullion and Alloys of Precious Metals

Denomination	Equivalent in milliemes or parts per 1,000	
1 k.	41.666	24 k. = 1 lb. troy (England) 24 k. = 1 mark (Germany, etc.)
1 grain per marc...	0.217	4,608 gr. = 1 marc of 8 oz. (France, Spain, etc.)
1 oz. per marc.....	125.000	8 oz. = 1 marc (France, Spain, etc.)
1 loth (silver)......	62.500	16 loth = 1 mark (Germany, etc.)

Conversion Tables—Weights

	Grains	Penny-weights	Troy ounces	Avoirdupois ounces	Avoirdupois pounds	Grams
1 grain.............	1	0.041666	0.0020833	0.00228571	0.000142857	0.0648
1 pennyweight	42	1	0.0500	0.0548571	0.00342857	1.5552
1 troy oz	480	20	1	1.0971428	0.0685714	31.104
1 avoirdupois oz ...	437.50	18.22917	0.911458	1	0.06250	28.35
1 avoirdupois lb	7,000	291.666	14.58333	16	1	453.60
1 mg	0.015432	0.000643	0.00003215	0.000035274	0.0000022046	0.0010
1 gram...........	15.432	0.643	0.03215	0.035274	0.0022046	1
1 kg..............	15,432	643	32.15	35.274	2.2046	1,000

Volume and Weight of Fine Gold and Silver

	1 cc.	1 cu. in.	1 cu. ft.
Fine silver:			
Weight: grams......	10.57	173.21	299,307
Weight: troy ounces	0.339825	5.5687	9,622.72
Fine gold:			
Weight: grams......	19.3	316.269	546,513
Weight: troy ounces	0.6205	10.1680	17,570.39

Table 1.—Pulp Formulas

d = density or specific gravity of dry solid (ore, sand, or slime).
p = specific gravity of pulp (mixture of water and ore, etc.).
S = percentage by weight of dry solid in pulp.
= grams in 100 g., tons in 100 tons weight, etc.
R = water ratio or dilution of pulp.
= tons water per ton of dry solid.
= grams water per gram of solid.
V = volume percentage of solid in pulp.
= cubic centimeters in 100 cc. pulp
= cubic feet in 100 cu. ft. pulp.
F = solid factor.
= grams solid in 100 cc. of pulp.

= tons solid in 100 fluid tons or 3200 cu. ft. of pulp.
= avoirdupois ounces in 0.1 cu. ft. of pulp.

k is a constant for any particular solid under consideration, used to facilitate calculation, and depending upon the density of the dry solid.

$$k = \frac{100d}{d - 1}$$

$$d = \frac{\quad}{1 - R(p - 1)} = \frac{Sp}{Sp - 100(p - 1)}$$

$$p = \frac{R + 1}{R + \frac{1}{d}} = \frac{100}{100 - \frac{S(d - 1)}{d}} = \frac{k}{k - S}$$

$$\frac{100}{R + 1} = \frac{100d(p - 1)}{p(d - 1)} = k(p - 1)$$

$$R = \frac{d - p}{d(p - 1)} = \frac{1 - \frac{p}{d}}{p - 1} = \frac{100 - S}{k}$$

$$\frac{100}{S} - 1 = \frac{100p}{k(p - 1)} - 1$$

$$F = Sp = \frac{100p}{R + 1} = \frac{100d(p - 1)}{d - 1} = k(p - 1)$$

$$V = \frac{F}{d} = \frac{Sp}{d} = \frac{100(p - 1)}{d - 1} = (k - 100)(p - 1)$$

$$\text{Volume percentage of water in pulp} = 100 - V = 100 - \frac{F}{d} = p(100 - S) = \frac{100(d - p)}{d - 1}$$

$$\text{Tons of dry solid per 100 tons water} = \frac{100}{R} = \frac{100S}{100 - S} = \frac{100d(p - 1)}{d - p}$$

$$\text{Fluid tons pulp to yield one ton solid} = \frac{100}{F} = \frac{100}{k(p - 1)} = \frac{R + 1}{p}$$

These formulas are strictly applicable only to mixtures of solids with liquids of specific gravity 1.00, such as water or cyanide solutions at ordinary temperatures.

Measurements of Daily Tonnage.—Several accurate methods are available; one depends on the direct weighing of the dried material caught during a measured interval of time; another on the measurement of time and the corresponding volume of pulp, together with the specific gravity of the pulp, using the known relations between the gravity and solid contents of pulp. Or one may estimate the flow of pulp by a weir or any other method and then determine the weight of solid in a measured volume. Reduced to the simplest terms, the computations from such data may be made by one or the other of the following formulas:

$$\text{Tons solid per day} = \frac{\text{pounds dry solid caught} \times 43.2}{\text{seconds observed}} = 43.2 \times \text{pounds per second}$$

$$\text{Tons solid per day} = \frac{2{,}700d}{d - 1} \times \frac{p - 1}{t}$$

This formula may be arranged for slide-rule calculation

where t = seconds required to yield 1 cu. ft. pulp.
p = specific gravity of pulp.
d = specific gravity of dry solid.
k = a constant for any particular material.

WATER AND SOLIDS IN PULP

	Weight pulp	Volume pulp	Weight dry solid	Weight water	Volume water
1 ton of pulp (2,000 lb.)	1 ton	$\frac{1}{p}$ fluid ton $\frac{32}{p}$ cu. ft.	$\frac{S}{100}$ ton $\frac{1}{R+1}$ ton $\frac{(p-1)k}{100p}$ ton	$\frac{d-p}{p(d-1)}$ ton	$\frac{d-p}{p(d-1)}$ fluid ton $\frac{32(d-p)}{p(d-1)}$ cu. ft.
1 fluid ton of pulp (32 cu. ft., 240 U. S. gal., 200 imp. gal.)	p tons	1 fluid ton 32 cu. ft.	$\frac{(p-1)k}{100}$ ton	$\frac{d-p}{d-1}$ ton	$\frac{d-p}{d-1}$ fluid ton $\frac{32(d-p)}{d-1}$ cu. ft.
1 cu. ft. of pulp (7.5 U. S. gal., 6.25 imp. gal.)	62.5p lb.	1 cu. ft. 0.03125 fluid ton	$0.625(p-1)k$ lb. $\frac{(p-1)k}{3200}$ ton	$\frac{62.5(d-p)}{d-1}$ lb. $\frac{d-p}{32(d-1)}$ ton	$\frac{d-p}{d-1}$ cu. ft.
1 ton of dry solid (2,000 lb.)	$R+1$ tons $\frac{100p}{(p-1)k}$ ton	$\frac{100}{(p-1)k}$ fluid ton $\frac{3200}{(p-1)k}$ cu. ft.	1 ton	R tons $\left(\frac{100}{S}-1\right)$ ton $\frac{d-p}{d(p-1)}$ ton	32R cu. ft. R fluid tons
1 fluid ton of water (32 cu. ft., 240 U. S. gal., 200 imp. gal.).	$\frac{p(d-1)}{d-p}$ ton	$\frac{d-1}{d-p}$ fluid ton	$\frac{1}{R}$ ton $\frac{d(p-1)}{d-p}$ ton $\frac{S}{100-S}$ ton	1 ton	1 fluid ton 32 cu. ft.

1 U. S. gal. of pulp $= \frac{(p-1)k}{12}$ lb. dry solid. 1 imp. gal. of pulp $= \frac{(p-1)k}{10}$ lb. dry solid.

METRIC VALUES.—The relation between the metric ton (of 1,000 kg.) and the cubic meter (1,000 liters) is identical with that existing between the ton of 2,000 lb. and the fluid ton of 32 cu. ft. For instance, 1 cu. m. of pulp contains $0.01(p-1)k$ metric ton dry solid.

k is a constant for any value of d. $k = \frac{100d}{d-1}$

$d =$	2.5	2.6	2.7	2.8	2.9	3.0
$k =$	166.7	162.5	158.8	155.5	152.6	150

$$\text{Tons solid per day} \quad \frac{(27k)(p-1)}{t}$$

$d =$	2.5	2.6	2.7	2.8	2.9	3.0
$27k =$	4500	4390	4290	4200	4120	4050

p may be obtained by a hydrometer in the case of slime pulp, or by weighing in grams the contents of a glass or tin liter flask, or by weighing in pounds the content of a bucket graduated to hold 100 lb. of water. (Such a bucket may be 14 in. in diameter and 20 in. deep, in which case the graduation for 100 lb. is about 18 in. from the bottom.) 100 lb. water = 1.6 cu. ft. The value of t may be observed with a stop watch in filling a 100-lb. bucket, but preferably with a much larger container.

$$\text{Tons solid per day} \quad \frac{\text{cubic feet per day} \times \text{pounds per cubic foot}}{2000}$$

CHAPTER XII

HYDROMETALLURGY OF COPPER

BY H. A. TOBELMANN[1]

Leaching is the term applied to the process of recovering a metal from an ore by a solvent or lixiviant and the removal of the resulting solution from the undissolved portion. In other words, leaching is the recovery of a metal from ore by a wet process.

In general, leaching is applied only to ores that are not adapted to treatment at an equal or greater profit by the longer established methods, such as gravity concentration, flotation, or smelting. It has not yet been applied on a large scale to copper ores containing a considerable quantity of precious metals, as the recovery of these is not high with the usual copper lixiviants. Its most extensive application so far has been in the treatment of low-grade oxidized ore, in which the copper is largely soluble in dilute sulphuric acid.

The oxidized copper minerals, such as the carbonates and silicates, are readily attacked by a number of the more common acids and alkalies while the nonoxidized or sulphide minerals are not and must first be prepared by roasting, weathering, or other means of oxidation, either with or without added chemical agents.

The leaching of copper ores can be carried out in the following ways: leaching in place, heap leaching, and confined leaching.

Leaching in Place.[2]—This method is based on the fact that, when an ore body containing sulphide is broken up so that both air and water have access to the ore, the sulphide portion of the mineral is decomposed and soluble sulphates are formed. The chemical reactions involved in this transformation of sulphides into oxidized forms have been discussed by Lindgren[1]. The behavior of sulphides of the same kind may be very different, oxidation sometimes not taking place for a long period and then again taking place so rapidly as to show decomposition within a few weeks. The more porous and more absorbent the gangue, the more rapidly will the ore respond to treatment. This method, which consists of treating ore without removing it from the mine, has been applied only to exhausted ore bodies and to mines containing large quantities of ore of such low copper content as to make its removal unprofitable, and in such a broken-up condition as to be provided with ample crevices for the circulation of both air and solution.

The action is very slow, but the method is inexpensive, the principal operating cost being the pumping and distribution of the solution and the iron and precipitation expense. The efficiency of the process in any particular case cannot be determined, as there is no known method of accurately determining the tonnage and copper contents either before or after operations.

The leaching results are obtained by the intermittent circulation of water and air through the crevices in the ore. One of the greatest difficulties of the process is that the slimes gathered from the ore and the accumulated salts may in time fill these crevices and temporarily, if not permanently, protect the exposed ore from further

[1] The chapter is a major revision by the editor of H. A. Tobelmann's original monograph.

[2] References in this chapter are to similarly numbered references in the Bibliography at the close of the chapter.

leaching action. Usually, the rate of extraction is quite rapid at first, but it decreases continually. The solutions from such an operation are nearly always impure, and precipitation of the copper by scrap iron is the only method that can be considered.

Leaching in place is neither new nor unusual and is recorded to have been successfully used on a small scale in Hungary during the fifteenth century. J. Parke Channing[2] states that copper was extracted by this process from the Eureka mine in the Ducktown district as early as 1850. According to Philip Argall[3], the Cronebane mine in Wicklow County, Ireland, was a good example of the application of this method. In this case numerous small drifts were driven immediately under the gossan, and water was introduced into the loose gossan on the surface. The solution, after being directed from one level to another through stopes and fillings, was pumped from the lowest level to the surface, where the copper was precipitated. Irving[4] refers to similar operation at the Aznalcollar mines in Spain. It has also been applied to some of the exhausted mines at the Rio Tinto[5]. The simplicity and the effectiveness of this method remained apparently unnoticed in the United States until the spring of 1923, when the Ohio Copper Co. of Utah[6] began the leaching of a large body, estimated to contain about 38,000,000 tons at 0.3 per cent copper, of thoroughly broken copper-bearing quartzite. The shattered quartzite itself was practically inert to chemical action, while the copper minerals existing principally in the fissures of this material were readily attacked by the leach solutions. Thus, there was little danger of clogging the ore body by decomposition or alteration products, as is so apt to occur in monzonite-porphyry ore bodies.

The operation consisted of carefully distributing on top of the caved ore area 1200 to 1500 gal. per min. of solution made up of about two-thirds fresh water and one-third launder tailings solution. The solution going on the ore averaged about 0.3 to 0.4 lb. of copper and 8 to 10 lb. of iron per thousand gallons. This solution percolated through the caved ore and was collected at the bottom of the shaft, where it was directed to the precipitation launders, situated on both sides of a large haulage tunnel. The solution entering the launders averaged about 15 to 20 lb. of copper and 2 to 3 lb. of iron per thousand gallons. There were two parallel launders, 32 in. by 32 in. by 1600 ft. long, in which 97 to 98 per cent of this copper was precipitated. Additional launders outside the haulage tunnel were provided to precipitate any remaining copper.

It will be noticed that iron was precipitated out of solution during its passage through the ore. This may have been due to hydrolysis or to the action of the ferric sulphate on the oxidized copper minerals in the ore, or both. Should this precipitation at any time seriously interfere with the percolation of solution, the further caving of a small quantity of ore, or acidulation of the water, would relieve this condition. It is of interest that solutions both going on and coming off the ore were practically neutral. Clean scrap was used and, due to the intelligent operation and supervision, an unusually high-grade precipitate was the result. The average precipitate produced by this company analyzed over 90 per cent copper, the impurities being those due to the entrained solution and consisting principally of iron and aluminum sulphates. The cement copper usually produced from such operations will average not over 70 per cent copper. The production of such a plant is necessarily largely dependent on the fresh water available. The Ohio Copper Co. consistently produced some 700,000 to 900,000 lb. of copper per month, or approximately 30,000 lb. per day. The total cost of operation has been published[7] as being 6 to 6½ cents per pound, f.o.b. New York, a cost that is rarely equaled. Of this amount, 50 per cent represented the pumping and precipitation costs.

Leaching of a mined-out area at Ray mines in Arizona was begun in January, 1937, using fresh water only as the lixiviant, and shredded tin scrap as the precipitant.

Precipitation should be carried on underground when conditions make it practical. The warmer the solutions, the more efficient both the leaching and the precipitation will be. Also, it is more difficult to pump solutions containing copper sulphate than those containing iron sulphate. Efficient precipitation cannot be accomplished with heavy scrap iron like car wheels, slag pots, and old rails, yet this is the practice generally tried, resulting in condemning the precipitation of copper by iron in general.

Heap Leaching.—This method of leaching is probably one of the oldest, if not the oldest, of the methods for the recovery of copper from ores. It is said to have been used as early as 1752[5] in recovering the copper from cuperiferous pyrite in Spain. This method, like the one first described, depends on the natural oxidation of the sulphide minerals by continual subjection to air and water. The chemistry of this oxidation has been much discussed, but still it is not accurately known[8].

Ores, both sulphide and mixed ore, which must be removed from the mine but which are too low grade to treat at a profit by any other method, can be treated by heap leaching. This is generally carried on as follows:

Ground with a slight slope is selected. It is cleared of any growths and is then rolled and packed with clay or slimes to make it as near waterproof as possible. Large boulders of ore are selected for building culverts and cross culverts for drainage and ventilation purposes, and the drainage is directed to a common point. The ore, without crushing or other preparation, is now carefully piled on this prepared area. In some cases, it has been found helpful to classify the material to the extent of placing the coarsest material on the bottom and the finest on the top as an aid to both the ventilation and the solution circulation. The top of the ore piles is provided with distributing trenches. Solution, consisting at first of fresh water and later of waste solution from which the copper has been precipitated, is directed over the ore pile. The wetting is so conducted that, while a certain section is being saturated with solution, other sections are permitted to heat and oxidize. In each passage of the solution through the ore, the sulphates that have formed from the oxidation of the sulphides are dissolved and washed away. The solution emerging from the bottom of the pile is directed to a sump, from which it is pumped to scrap-iron precipitation launders, where the copper is recovered as cement copper. The solution with the copper removed is pumped back to the ore for further leaching.

The method is quite simple, but the reaction is very slow. As years are required to obtain a commercial extraction, this method can be profitably applied only to very large tonnages. The principal method of recovering copper at Rio Tinto has been by a heap-leaching process. Two classes of ore are leached by this method, a pyrite and a quartz. When leaching sulphides, the fines and the coarse are treated together. The heaps are 10 to 40 ft. high. The tops are divided into squares for better solution distribution. According to De Kalb[5], at one time there were about 20,000,000 tons, occupying about 350 acres, undergoing treatment. The heaps have been placed on a gently sloping hillside having a naturally impervious floor. About 150 gal. of solution per ton of ore per year is required. About 60 per cent extraction is generally made in the first 3 years, while 7 to 9 years is required to bring this up to 80 or 85 per cent. It is also said that some of these piles have been under treatment for nearly thirty years. The pyrite itself is barely attacked and is sold for its sulphur value.

Some data are also available on operations at Sacramento Hill, Bisbee, where heaps containing over 1,800,000 tons of ore were leached. In the first 21 months, 37.28 per cent of the copper was extracted at a cost of about 5.5 cents per pound. The loss of, and absorption of, water amounted to 24¼ per cent of the total sent to the heap. The first heap (750 × 1800 ft. base) had an analysis of Cu, 0.92 per cent; SiO_2, 63.5 per cent; Al_2O_3, 11.2 per cent; CaO, 0.7 per cent; S, 6.8 per cent[51].

In leaching the old waste dumps at Tyrone, New Mexico, it was found necessary to direct the leaching water into the dumps under pressure. If this was not done there was channeling, and test pits showed unleached portions. Oxidation appeared accelerated by alternate wetting and drying. Baled factory scrap was found the most satisfactory precipitating base. About 1.30 lb. was consumed per pound of copper recovered[52].

Heap roasting followed by subsequent heap leaching has been practiced. Schnäbel speaks of a process at Rio Tinto which consisted of slowly roasting elliptical heaps of sulphides containing some 1500 tons of ore. After roasting, the pile was leached with water, whereupon the larger portion of the copper was recovered. The partially leached ore was now restacked over horizontal flues to permit of thorough ventilation and was moistened from time to time, whereby much of the remaining copper was recovered. The copper was precipitated by iron.

Confined Leaching.—By "confined leaching," the leaching of an ore in tanks or vats is meant. This may be accomplished in two ways, either by agitation or by solution circulation, depending largely on whether or not the ore must be finely ground to give a profitable extraction. This form of leaching may be divided into the following principal operations: (1) reduction to size, meaning the necessary crushing, grinding, and screening; (2) the converting of the copper mineral to an oxide or sulphate by roasting or otherwise, if it exists in a nonoxidized form; (3) dissolving the copper in the cheapest and most suitable reagent and removing the resultant solution from the undissolved portion of the ore; (4) washing the treated ore so as to recover the entrained copper solution; (5) the precipitation or removal of the copper from these pregnant solutions.

Reduction to Size.—The fineness to which an ore will have to be crushed to give a commercial extraction is largely dependent on its porosity, the size of the mineral grain, the degree of dissemination, and the rapidity with which the mineral is attacked by the lixiviant used.

In most cases where copper ores are treated by leaching, the mineral exists as seams or filling of fissures, and fine grinding is resorted to only when rapid extraction is desirable or necessary. Rarely, however, is the copper-bearing mineral so disseminated and so surrounded by an impervious gangue that fine grinding is necessary for releasing the mineral particles in order to give access to the solvent. The typical material leached at Chuquicamata is an example of the copper mineral occurring in seams and the filling of fissures, whereas the material treated at Ajo would be an example of the more distributed copper minerals.

The influence of screen size on extraction can be seen from the table on page 349. This table shows the mesh, the percentage of copper in heads and in tailings, and the extraction on material of the different mesh for the year 1920 at the New Cornelia Copper Co.'s plant at Ajo, Ariz.[10]. During this year sizing tests were made of each head and tailing sample, composited monthly and analyzed. The average for the year was then computed.

The coarser the mesh that can be leached, the less will be the crushing expenses and the more efficient the circulation. As the time required to leach an ore depends almost entirely on the solution penetration, it can be seen that the larger the particle of ore, the longer the time that will be required to dissolve the copper. The treatment of coarse material entails less expense not only as to crushing, but it is simpler to remove the dissolved copper, there is less copper entrained in the final material discarded, and less impurities will be dissolved per unit acid neutralized. Coarse grinding will permit leaching by percolation in tanks in which the material is stationary and the lixiviant moving, so that leaching and removal of the dissolved copper from the gangue are coincident.

Distribution of Copper in the Ajo Heads and Tails

Heads, per Cent Copper

Mesh	Per cent	Total	Oxide	Sulphide (by difference)	Soluble	Insoluble (by difference)
On 3	26.6	1.37	1.23	0.14	1.28	0.09
On 4	18.6	1.33	1.18	0.15	1.23	0.10
On 6	13.2	1.39	1.25	0.14	1.30	0.09
On 8	9.1	1.46	1.30	0.16	1.34	0.12
On 10	6.4	1.55	1.39	0.16	1.43	0.12
On 14	5.0	1.62	1 46	0 16	1.49	0.13
On 20	3.1	1.75	1.57	0.18	1.62	0.13
Through 20	18.0	2.06	1 82	0 24	1 88	0.18
Calculated	100.0	1.534	1.368	0.167	1 416	0.118

Tailings, per Cent Copper

Mesh	Per cent	Total	Oxide	Sulphide (by difference)	Soluble	Insoluble (by difference)
On 3	25.8	0.47	0.35	0.12	0.37	0.10
On 4	20.1	0.32	0.21	0 10	0.23	0.09
On 6	12 5	0.25	0 14	0 11	0.15	0.10
On 8	8.7	0.21	0.10	0.10	0.11	0.10
On 10	7.2	0 21	0 09	0.12	0.10	0.11
On 14	4 8	0 21	0 11	0.10	0.11	0.10
On 20	3 8	0.22	0 11	0.11	0 12	0.10
Through 20	17 1	0.35	0 19	0 16	0.18	0 17
Calculated	...	0.328	0.210	0.122	0.223	0 110

Per Cent Extractions

Mesh	On total copper	On oxide copper	On sulphide copper	On soluble copper
On 3	65.69	71.5	14.3	71.1
On 4	76.00	82.2	16.5	81.3
On 6	82.03	88.8	21.4	88.5
On 8	85.62	92.3	31.3	91.8
On 10	86.45	92.8	25.0	93.0
On 14	87.04	92.4	37.4	92.6
On 20	87.43	93.0	38.8	92.6
Through 20	83.01	90.2	29.2	90.4
Calculated	78.50	84.9	27.0	84.3

In treating coarse material, it is very important to have as much of the material of the same mesh as is practical, as oversize will not be leached and fines will interfere with solution percolation. The necessity of a uniform product for consistent extractions resulted in the adoption of disk crushers[11] at Ajo.

As a rule, the richer the material to be leached, the finer the grinding necessary for economical extraction. However, the smaller the mesh, the greater the quantity of slimes produced and the less efficient will be leaching in tanks. Slimes, when present, cause channeling, which prevents even distribution of solution and interferes with uniform extraction. When fine grinding is resorted to, the material must be classified and the sands and slimes separately treated. Where no classification and separate treatment is feasible, the product must carry the minimum quantity of fines to prevent interference with percolation.

When finely divided material is leached, both the solids and the solution are moving and the separation is accomplished by the standard methods of settling, decanting, and filtering. Probably the coarsest material being treated by a leaching process in tanks and by circulation is at Chuquicamata, where 90 per cent of the material is crushed to pass a 0.371-in. screen. At Ajo about 27 per cent remains on the 0.261-in., or approximately ¼-in., screen.

The importance of proper crushing may be seen by the following: If the ore leached at Ajo had been so crushed that the material remaining on 3 mesh were crushed to pass 3 mesh but not to pass 4 mesh, the extraction would have been increased a little more than 2 per cent, or approximately 0.6 lb. of copper per ton of ore.

In any form of leaching, whether with an acid or an alkali solvent, slimes must be avoided as much as possible.

Oxidation or Roasting of Sulphides.—As has already been stated, copper in an oxidized form is quite soluble, while in the sulphide form it is not. Roasting, which is essentially oxidation, is resorted to, and ores that are proposed to be treated by a wet process and that consist of all or part sulphides must be roasted.

During roasting, sulphides are not only oxidized or converted to sulphates but under proper conditions a large part of undesirable elements, like arsenic, antimony, and bismuth, can be volatilized. Heat-treatment, such as roasting or thorough dehydrating, is an advantage to many ores, making the impurities less soluble and leaching and filtration less difficult.

To obtain the best results, the proper roasting conditions must be determined for each ore. The literature on the subject is extensive and covers a great many different conditions. It has been found possible under proper conditions so to roast an ore as to convert practically the total copper present in a mixed ore to a water-soluble sulphate[12].

Roasting is frequently carried on in the presence of, or with the aid of, a reagent, usually sodium chloride, or common salt, with the object of converting the copper into a more soluble chloride and the silver into a more soluble compound. Roasting with sodium chloride, however, requires careful regulation of temperature, since, under certain conditions of temperature and certain ratios of salt and sulphur, the copper may be almost completely volatilized (see Chap. XVII, Chlorine in Metallurgy).

Dissolving the Copper.—Many lixiviants have been proposed for dissolving the copper in an ore. These include both acid and alkalies and are, in order of their importance, sulphuric acid, ammonia and ammonium carbonate, ferric sulphate, sulphurous acid, ferric chloride, cupric chloride, hydrochloric acid, chlorine, and nitric acid.

Of these, sulphuric acid is the cheapest and the solvent most commonly used. It reacts readily with the oxidized copper minerals, forming copper sulphate. Its action on the copper sulphide minerals is practically negligible. It is, unfortunately,

also a ready solvent for many other constituents of ores in which the copper minerals occur—in some cases, to such an extent that it cannot be profitably used. It is always used as a dilute solution, probably never exceeding 10 per cent and seldom exceeding 5 per cent, depending upon the grade of the ore, the time of contact, and the temperature of the lixiviant. Sulphuric acid has a selective action for copper and in very dilute solution will react with copper in preference to the other constituents of the ore.

It has long been recognized that in the leaching of copper ores, as in cyaniding gold ores, the product of the time of contact and the solution concentration is a constant. In other words, if a given ore is leached on a given mesh for 8 days with an average acid concentration of, say, 2.5 per cent, the same extraction will be obtained as when leaching this material 16 days with half the acid concentration, or 1.3 per cent. The important fact, however, is that in the case of the greater concentration only 50 per cent of the acid was used in dissolving copper, while more than 75 per cent was used when using the lower acid concentration. In other words, the lower the acid concentration, the less impurities will be dissolved. In leaching with sulphuric acid, the acid is one of the largest, if not the largest, item of expense, and when electrolysis is used to precipitate the copper, much of the acid combined with elements other than copper is permanently lost. Impurities are objectionable not alone from the point of excessive acid consumption, but also because of their accumulation when the method of precipitation is such that the solution may again be used. Also, impurities may accumulate in a solution to such a point that it will be no longer efficient and it will have to be discarded. The largest leaching plants operated, Chile Copper Co. at Chuquicamata, the now abandoned New Cornelia Copper Co. plant at Ajo, Ariz., and Andes Copper, at Potrerillos, used dilute sulphuric acid as the leaching agent.

The subject of sulphuric acid leaching processes would not be complete without reference to the excellent process devised by Greenawalt[29]. While this process is very similar in many respects to that used at Ajo, each was developed independently. The Greenawalt process has two outstanding features. These are (1) the continuous reduction of the ferric sulphate with sulphur dioxide by circulating the cell solution in closed circuit with the reducing apparatus; (2) the precipitation of the copper in the discard solution by means of hydrogen sulphide instead of with scrap iron as at Ajo.

This process is applicable to oxidized as well as to roasted sulphide ores. By this continuous reduction feature, Greenawalt states that he is able to reduce the copper content of the solution going through the electrolytic cell to a greater degree than with simple reduction as carried on at Ajo.

For the removal of the copper from the solution that must be discarded, Greenawalt uses hydrogen sulphide. This is effective in various acid concentrations and has the advantage of leaving the solution in condition for further use as a lixiviant should this be desired. It is very doubtful, however, if the cost of the precipitation of the copper from waste solutions by hydrogen sulphide is less expensive than precipitation by scrap iron. From tests conducted at Ajo, the costs are about the same, while the solubility of the copper sulphide precipitate in dilute ferric sulphate is not appreciably different from that of cement copper.

The main feature of the Greenawalt process is the continual generation of sulphuric acid. The process, when operated under proper conditions, may be made self-sustaining. As the cost of sulphuric acid is one of the largest items of expense in leaching, the advantages of this process may readily be seen.

At Ajo, where the ferric sulphate in the solution going to the electrolytic cells was reduced with sulphur dioxide, there were periods when the sulphuric acid produced in the towers alone was sufficient to carry on the leaching process.

Ammonia and Ammonium Carbonate.—Next to sulphuric acid in importance and efficiency as a leaching agent may be mentioned ammonia and ammonia compounds. In the presence of air, ammonia and ammonia salts react quite energetically with metallic copper and oxidized copper compounds. The active constituent is the cupric ammonium carbonate that is formed and which reacts with the copper minerals, forming cuprous-ammonium carbonate. In the presence of air, the cuprous compound is rapidly oxidized to cupric, and again becomes an active leaching agent. When a solution containing cuprous or cupric ammonium carbonate is heated, both the ammonia and the carbonic acid are distilled off and condensed while the copper is precipitated as a cuprous or cupric oxide. There is no fouling of solution.

This process is said to have been originally developed in Germany[13, 14]. In 1871, in a paper read before the A.I.M.E., the matter of native-copper losses in the Calumet & Hecla tailings was discussed and the fact brought out that this copper could be dissolved in solutions of ammonia salts. Some years later when the treatment of these tailings was again considered, ammonia-leaching tests were conducted which resulted in the erection and operation of the present plant, in which some 8000 tons per day is treated.

The material treated at the Calumet plant is finely divided metallic copper in sands. This metallic copper is at all times covered with a thin film of oxide which is rapidly dissolved in ammonia in the presence of an ammonia salt. If the metallic copper is again subjected to the air, it will again be covered with a thin film of oxide which will dissolve. These reactions are the basis of the ammonia-leaching process.

The early difficulties of the process are said to have been the loss of the highly volatile ammonia which occurred both during the leaching and during the boiling of the solution. Benedict[13] found that this loss was not solely due to volatilization but to a larger extent to adsorption of ammonia by the ore particles. This loss increased with the strength of solution. By using only a weak solution, treating low-grade material, and driving off the adsorbed ammonia from the tailings by steam before discharging, Benedict found that these losses could be reduced to a minimum. This process when applied to the Calumet tailings gives an average extraction of about 80 per cent.

At the Kennecott Copper Corp. at Kennecott, Alaska[15, 16], copper carbonate, both azurite and malachite, occurred with chalcocite in dolomite and limestone. The ore was treated by milling, whereby most of the sulphide copper and about 60 per cent of the oxidized copper mineral are recovered.

The tailings from the milling process were screened at 20 mesh, the undersize going to tables and the oversize to Hancock jigs. The tailings from the coarse tables and jigs furnished the leaching-plant head, while the fine sand and slime-table tailings were treated by flotation.

The original lixiviant contained about 6 per cent NH_3, but owing to the success of washing the ore with low-pressure live steam, concentrations of as high as 11 per cent were eventually successfully used. Much difficulty was at first experienced with corrosion of iron and steel evaporator equipment by ammonia vapor. Aluminum was substituted in the condensers and concrete in the storage tanks. The ammonia loss, after the introduction of the live-steam wash, was cut to 0.45 to 0.60 lb. NH_3 per ton of ore treated. Steam consumed was about 220 lb. per ton of ore, 55 per cent in the evaporators, 45 per cent in the steam wash. Multiple-effect evaporation was used.

An ammonia process known as the Perkins process[15] is said to have given excellent results on some of the low-grade ores of the Southwest. This process consists of heating the ore to be leached in a reducing atmosphere, during which all or a large

part of the copper mineral is converted into metallic copper. It is then leached with ammonia.

Ferric Sulphate.—Ferric sulphate is not only an active solvent of most oxidized copper minerals, but also quite an active solvent of free copper sulphides. Complete extraction is possible on oxides and on carbonates in comparatively short periods, while sulphides are more slowly acted upon. To overcome the resistance of double sulphides, such as chalcopyrite and bornite, to this reagent, a partial roasting was suggested by Thomas. This was found very helpful, and under proper roasting conditions commercial extraction may be obtained from sulphide ores with ferric sulphate as the lixiviant. Heat was found to promote the leaching reaction.

Much careful work has been done with this reagent. Probably the earliest is that of Siemens & Halske, who, in 1890, introduced a process that consisted of leaching an ore ground to 90 mesh with hot dilute ferric sulphate. The copper was precipitated electrolytically, using insoluble anodes and the lixiviant regenerated. The results obtained by Siemens & Halske were disappointing and did not warrant its further introduction. This work, however, is the basis of most ferric sulphate processes. There is no doubt that, had there been available to these investigators the present knowledge of the use of insoluble anodes, diaphragms, tank linings, etc., the results would have been very different.

Among the large-scale tests made with this reagent, probably the more important are those made at Cananea, Sonora, by the Cananea Consolidated Copper Co.[24] and at Ray, Ariz., by Westervelt[24]. At Cananea the principal difficulty encountered appeared to be the regeneration of the lixiviant. At Ray, the raw ore was leached with hot dilute ferric sulphate and the copper was precipitated electrolytically. This later work was practically a modification of the Siemens & Halske process, and, as at Cananea, the regeneration of the solvent appeared to be the principal difficulty.

In heap leaching, as practiced at Rio Tinto, where copper is extracted from massive iron pyrite, the extraction depends upon the action of ferric sulphate. By proper control of the ventilation and the wetting of this ore, ferrous sulphate is formed, which, on further action, changes to ferric sulphate and, as such, dissolves the copper.

Sulphur Dioxide.—Sulphur dioxide is readily absorbed by water, forming sulphurous acid. As such, it is an active solvent of many oxidized copper compounds. It can generally be cheaply and easily secured, as nearly all districts containing copper also contain some sulphur.

Ore containing high acid-soluble constituents are especially adaptable to sulphur dioxide leaching. Copper sulphite is formed. This is unstable and is readily converted into cuprocupric sulphite and copper sulphate. Cuprocupric sulphite is slightly soluble in water, but is easily soluble in sulphur dioxide and in cupric sulphate.

The use of sulphur dioxide as a leaching reagent has been very attractive, with the result that much experimenting has been done and many processes have been devised. Of these processes the earliest one is probably that of Neill and Burfiend, a patent for which was issued about June, 1902. This process consisted of subjecting the ore to the action of sulphur dioxide to dissolve the copper, removing the solution from the ore and then heating it to drive off the excess of sulphurous acid and precipitate the copper as sulphite.

The process was given a rather extensive trial on the sandstone copper ores of northwestern Arizona[18], but the work was discontinued before the value of the process was definitely established. The instability of the copper compounds appeared to be the principal difficulty. Joseph Irving, Jr.[23], describes some leaching tests made at the Nevada-Douglas Consolidated Copper Co., where wetted fine ore was brought in contact with hot sulphur dioxide gas. The copper was precipitated upon scrap iron. The process was devised by G. C. Westby and S. S. Sorenson.

Many other commercial or near commercial tests were made along similar lines, but up to this time (1942) there are no large installations of this kind either in process of construction or in operation. That this reagent has many attractive possibilities is, however, generally conceded.

This problem was taken up and seriously studied during 1917 and 1918 by the U. S. Bureau of Mines[19]. It was thought that a successful process, compact and apparently inexpensive, had been developed. The operations were simple and readily controlled. They consisted of passing a mixed ore pulp through a revolving drum containing baffles to impede the progress of the ore, countercurrent to hot sulphur dioxide gas. The copper was brought into solution during the passage of the pulp through the drum, and was later recovered either by precipitation on iron direct, or by precipitation on iron and then floating the metallic copper precipitate.

During the development of this process[20], it was found that the pulp from the treatment of a roasted cupriferous pyrite by this process contained an unexpected quantity of free sulphuric acid. Careful investigation brought out the fact that dilute sulphur dioxide gas had a tendency to oxidize the ferrous sulphate to the ferric state and produce free sulphuric acid. In other words, when ferrous sulphate is agitated under certain conditions with air and sulphur dioxide, the ferrous sulphate is oxidized to ferric and free acid is produced. It was found that the free acid concentration so produced could be carried to as high as 5 per cent.

Chlorides.—Of the various chlorides that have been suggested, ferric chloride is probably the most important, on account of its cheapness and the ease with which it may be regenerated. It not only has the property of readily dissolving the oxides of copper, but it quite actively decomposes many of the sulphides of copper. Its application as a leaching reagent for copper ores was mentioned as early as 1859.

Ferric chloride, while similar to ferric sulphate in its effect on copper ores, is less apt to form basic salts, and attacks other elements more readily. Cupric or cuprous chlorides are formed by the action of ferric chloride on copper sulphides, the ferric chloride being reduced to ferrous, and, as such, may be regenerated by chlorine.

The Doetsch process, based upon the reaction between ferric chloride and copper sulphides, was once extensively used at Rio Tinto. This process consisted of leaching large heaps of half-inch ore, previously mixed with salt and ferrous sulphate, with a dilute solution of ferric chloride. The ferrous chloride produced during the leaching was converted to ferric by bringing the solution in contact with chlorine gas, in scrubbing towers.

The Froelich process consists of agitating finely ground ore with a warm ferric chloride solution and precipitating the copper with metallic iron.

Both processes have merit and warrant further investigation.

Ferrous chloride has also been used to some extent as a leaching agent. The most notable application of this lixiviant is in the Hunt & Douglas process[25]. Roasted or oxidized ores were treated with a neutral solution of ferrous chloride and sodium sulphate. As this reagent does not dissolve arsenic, antimony, and various other elements highly objectionable to copper, the precipitate was very pure. This method was later somewhat modified, and a comparatively large tonnage of material for that time was treated by this process.

The Hoepfner process, in which cupric chloride was used as a lixiviant, at one time received much attention. The copper is precipitated electrolytically from a cuprous chloride solution; the cupric chloride which is formed during deposition, is used as the solvent for further copper. The principal obstacles to the success of this process were the tendency of the cupric chloride to dissolve the deposited copper and the necessity of continual solution purification.

Chloridizing, roasting, and leaching have found quite wide application as the Longmaid-Henderson[35] process, which is at the present time the principal process employed in recovering copper from pyrites cinders. The crushed cinders mixed with salt and sometimes with pyrite are treated in special muffle furnaces. The material so treated is then discharged into tanks and leached with water, precipitating the copper with iron.

The advantage of chlorine as a reagent has long been recognized, and its intensive action on the ores of the various metals has been also investigated. The principal obstacles in the use of this reagent are mostly mechanical and not chemical. The application of chlorine will find its greatest field in ores carrying, besides copper, precious metal values.

Nitric Acid.—The proposal to use nitric acid as a leaching agent is quite old, dating back at least to 1874. The fundamental idea is to employ the nitric acid as a catalyzer to obtain a complete oxidation of the sulphides to sulphates by means of atmospheric oxygen at a comparatively low temperature. The use of nitric acid for decomposing sulphide ores in analytical work is old. It has been proposed to feed finely crushed ore, with the proper proportion of nitric acid, into a rotating furnace, similar to a cement kiln, which is heated near the lower end to a temperature sufficient to expel completely the nitric acid and the oxides of nitrogen after the sulphating reaction is completed. The presence of sulphuric acid derived from the pyritic sulphur will assist the decomposition of any nitrates that may be formed. The sulphated ore was to be leached in the usual way. The nitric acid vapor and lower oxides of nitrogen were to be recovered by a suitable tower and scrubbing system, and converted through the agency of atmospheric oxygen and water into nitric acid. The nitric acid required is directly proportional to the quantity of sulphides in the ore.

The success of this process depends upon minimizing the loss of the nitric acid which may occur in three ways, *viz.*, through the formation of nitrous oxide and free nitrogen, which cannot readily be converted into nitric acid; through the incomplete expulsion of nitrogen compounds from the sulphated ore; and through leakage and inefficiency of the recovery system.

The use of nitric acid as a leaching agent under certain conditions has been patented at various times. Of these, the Rankin process[21], in which ore is treated with nitric acid in a closed vessel with temperature not over 125°C., is probably the best known. This process was tried out at the Nevada Douglas Copper Co., Ludwig, Nev.[22].

From all accounts, the nitric acid process seems worthy of consideration, particularly for the treatment of low-grade sulphides as well as low-grade ore containing both oxides and sulphides.

Nitric acid is probably the most active of all solvents for copper ore and will energetically attack both the oxides and the sulphides, but the successful operation of this process will depend upon being able to obtain a high percentage recovery of this rather expensive reagent so as to distribute the cost over sufficient copper to make the process commercial.

Washing.—After the copper values have been dissolved from the ore and the solution drained off, there is still present a large quantity of dissolved copper as entrained solution. In some cases this entrained solution may amount to between one-half to one-third of the total copper dissolved from the ore. When an ore has been leached by percolation, this dissolved copper may be recovered in either of two ways: (1) by filling the interstices with water and circulating this water, draining, and repeating this operation until the entrained copper is negligible; (2) by filling the interstices of the ore with water and then drawing it off at the bottom, keeping the

material covered and the interstices filled until the draining shows a negligible quantity of copper. This latter method is called the "piston method." It is claimed to use less water, require less time, and cause less trouble than the first method. The former is the method used at Ajo, the latter is the method used at Chuquicamata.

Precipitation.—The methods of precipitating copper from the pregnant acid or neutral solutions are, in the order of their importance: (1) precipitation as the purest form of copper by electrolysis, usually from copper sulphate electrolyte; (2) precipitation as impure metallic copper by some form of metallic iron from sulphate or chloride solutions; (3) precipitation as metallic copper with sulphur dioxide under heat and pressure when applied to sulphate solutions; (4) precipitation with hydrogen sulphide as copper sulphide.

In the processes in which ammonia and ammonium carbonate are used as a lixiviant, the copper is precipitated out of solution by simply boiling off the ammonia. At the present time, the first two, only, are of commercial importance in the treatment of pregnant solutions obtained from acid lixiviants.

Precipitation by electrolysis is very similar to electrolytic copper refining. The principal difference is that in the former case insoluble anodes are used and the copper is taken out of the solution, while in the latter case the anodes are soluble and replenish the copper contents of the electrolyte as it is withdrawn.

The resulting product, electrolytic cathodes, is the purest obtainable commercial copper, is easily handled, and has only to be melted into shapes to meet commercial requirements. The impurities occurring in refinery solutions are generally more serious than those existing in leaching solutions. Refinery electrolytes are frequently apt to contain arsenic and antimony in quantities sufficient to contaminate the copper. None of the leaching solutions treated at the present time by electrolysis contain appreciable quantities of arsenic or antimony. The impurities that do occur in leaching solutions are readily eliminated by simple fusion.

Copper has been precipitated from chloride and other electrolytes, but not on a large enough scale to warrant discussion. Probably all the copper sulphate leaching solutions containing over a certain percentage of copper can be prepared for electrolysis. Its application will depend almost entirely on the cost of power.

Alumina, iron, magnesia, and sodium are the principal elements besides copper that occur in leaching-solution electrolytes. Of these impurities, the iron, on account of its alternate oxidation and reduction, thereby uselessly consuming current, is the most important one.

When electrolysis is used to precipitate copper from solution, the acid that was combined with the copper is regenerated. The impurities, however, accumulate and must be removed.

This ferric sulphate problem may be remedied in three ways: (1) by the use of a diaphragm or porous partition, so that the ferrous iron that is oxidized at the anode cannot come in contact with the deposited copper at the cathode; (2) by purification of the solution previous to electrolysis; (3) by keeping the ferric sulphate contents of the electrolyte at as low a point as is possible by continual reduction with sulphur dioxide.

The use of a diaphragm anode as a method of solving the ferric sulphate problem has not been applied on a large scale, principally because no satisfactory commercial diaphragm has yet been developed. While the advantages of a properly constructed diaphragm would be very important, its use would probably be limited to cases in which ferric sulphate is to play the more important part as a leaching agent, as with the simple sulphides of copper.

Purification of solution is commercially practical. Such a method, based on the Ottokar Hoffman[26] process of purifying copper sulphate solutions and applied to the

treatment of leach solutions, was tried at Ajo. This process, invented by Pope and Hahn[27], consisted of treating the ore with two lixiviants, a low and a high acid. The former dissolved much copper and few impurities, the later dissolved the balance of the copper and a greater quantity of impurities. The later solution was purified by heating, and then agitating with air after the addition of sufficient roasted copper concentrates, to precipitate the iron. The solution is filtered, the filtrate is added to the first leach liquor, and both are electrolyzed. Between 75 and 85 per cent of the total impurities in the electrolyte were removed. These tests were discontinued before the value of this process was definitely proved.

The reduction of the ferric sulphate by sulphur dioxide is very simple and is no doubt the cheapest and most efficient way to meet this problem. Its use for such a purpose is not new, having been suggested as far back as 1908.

The application of sulphur dioxide for this purpose on a large scale was quite openly ridiculed. As late as 1914, the engineers on the New Cornelia Copper Co. test plant were advised that reduction with sulphur dioxide on a commercial scale was impossible and were urged to give up this matter. No trouble was experienced except that it was found that, as may be expected, the more nearly neutral a solution is, the more easily it may be reduced.

Sulphur dioxide is cheap, the application for reduction is simple, and for each pound of sulphur used in reducing ferric sulphate 3.5 lb. of free sulphuric acid is produced. About 30 to 35 tons per day of ferric sulphate is reduced to ferrous sulphate with sulphur dioxide in the reduction towers of the New Cornelia Copper Co. To obtain this result, some 35 to 40 tons of sulphide ore containing 40 per cent sulphur is roasted to a calcine containing about 6 per cent sulphur. During this operation about a hundred tons of free sulphuric acid is regenerated, or about 75 per cent of the total required by the leaching plant. Under proper conditions the acid produced by the ferric sulphate reduction will be sufficient to carry on the process without the addition of acid from other sources.

The sulphur contents of the gas employed in reduction is not of vital importance, although, naturally, the higher the SO_2, the more efficient will be the absorption. The gas used at Ajo was as low as 3 per cent and as high as 8 per cent, with an average of about 5½ per cent for 6 years of operation. The use of towers for reduction proved satisfactory. For the entire 6 years, the ferric sulphate contents of the solution entering the electrolytic tank house averaged 0.10 per cent or less, while for 4 years the average was less than 0.05 per cent.

Greenawalt appears to have somewhat improved the process of intermittent reduction as used at Ajo by connecting each set of depositing cells with a sulphur dioxide reducing apparatus. In this manner, the ferric sulphate is reduced nearly as fast as it forms, and the continually increasing acid contents to some extent compensate for the decreased copper contents in the resistance of the cell, and more copper can be deposited per cycle than at Ajo.

In the Greenawalt process rapidly revolving disks, the peripheries of which just touch the surface of the solution and thereby produce a continuous quantity of exceedingly fine spray, are used in place of towers for reducing purposes.

The electrolysis may be carried on in either lead-lined or asphalt tanks. The former are used at Ajo, the latter at Chuquicamata.

Lead anodes are used where the solutions contain neither chlorides nor nitrates. After 6 years of continuous operation the antimonial-lead anodes in use at Ajo showed but little loss in weight.

Carbon or graphite anodes have not been used on a commercial scale for this purpose. One pound of copper per kilowatt-hour has been the average efficiency obtained when using lead or antimonial lead anodes.

Iron Precipitation.—In solutions of low copper concentration, too high in impurities for electrodeposition, some form of iron is generally used for precipitation purposes. When metallic iron is immersed in a solution containing copper, the iron is dissolved and metallic copper is precipitated. The product of this reaction is known as "cement copper."

Metallic iron has many advantages as a precipitant: it is generally quite cheap, readily obtainable, and simple to use. Clean iron as a precipitant will, with proper operating care and conditions, produce a high-grade precipitate. The usual 30 to 60 per cent copper contents of cement copper is neither necessary nor is it good practice.

There is theoretically required 0.878 lb. of iron per pound of copper to be precipitated, provided no other iron-consuming constituent is present in the solution. Both ferric sulphate, by its reduction to ferrous sulphate, and sulphuric acid, by its action to form ferrous sulphate, consume iron when present in the solution.

Due to the impurities of the iron, consisting of the constituents of the metal other than iron and the adhering iron oxide scale which is nearly always present, as well as the iron-consuming constituents of the solution from which the copper is precipitated, the consumption of iron per pound of copper is generally about 1.5 to 2.0 lb. instead of the theoretical 0.88 lb.

For good precipitation purposes, the solutions should be of as low density as possible; they should be clear, *i.e.*, all sand and slimes should have been settled out; the iron should be of as good grade as possible, and clean. The speed with which the reaction takes place depends, of course, upon the surface of iron exposed to solution. Pig iron acts the slowest and sponge or powdered iron the quickest. Therefore much work has been done on the development of sponge-iron process. This process would consist of reducing the iron in iron ore to metal in a finely divided state and without fusion.

The most important results were obtained at the Chino Copper Co., where a special furnace was developed for continuously producing sponge iron[39]. Here a magnetite concentrate was heated with a partly coked coal in a gastight furnace in which the charge was heated by radiation.

After the development of this furnace, the U. S. Bureau of Mines announced the development of a similar process, the reduction, however, taking place in a revolving Bruckner-type furnace, very similar to that used at Anaconda also for sponge-iron tests.

Notwithstanding the fact that much work has been done on sponge iron, there are, with the possible exception of some Second World War developments, no plants in successful and continuous commercial operation at this time.

Both heat and agitation are aids to precipitation. Fine material, such as sponge or shot iron, will permit of agitation, while precipitation with loose or baled scrap, or with pig iron, must be carried on in launders.

With a clean detinned scrap iron, the Ohio Copper Co. produced some millions of pounds of cement copper, which averaged over 90 per cent of copper. Several lots, consisting of 50 or more tons each, averaged over 95 per cent copper. These are the results obtained when using clean solution of low density and with proper supervision. The average copper contents of all the cement copper produced at Rio Tinto, where pig iron is used, is 75 per cent. At New Cornelia, where baled scrap is used, it is 60 to 65 per cent.

The chemical precipitation of copper by iron is nearly always carried on in either a sulphate or a chloride solution. In either case, it is quite necessary to reduce the ferric salts before precipitation. This may be done by passing the solution over copper or iron sulphides.

The statement frequently made that the acid must be neutralized before the copper will precipitate is not entirely correct. Precipitating copper from waste solutions on

scrap iron is frequently done at copper refineries. These solutions sometimes contain as much as 15 per cent acid, and the copper may be entirely precipitated without complete or nearly complete neutralization of the acid.

The cement copper commercially produced contains 20 to 30 per cent water or solution. Where this material has to be transported a long distance, drying might prove economical. When drying the material, however, it oxidizes. When it is very dry, it causes trouble by dusting. Tests on drying cement copper showed, when slowly dried to 15 per cent moisture, that 60 to 70 per cent of the copper contents had been oxidized. Whether dried in air or by heat, the quantity of copper oxidized appeared about the same. Air drying is too slow to be commercial. Drying with moderate heat is probably best. The statement that cement copper in drying oxidizes so quickly as to cause spontaneous combustion could not be proved.

The disposal of this cement copper has been the cause of much discussion. Producers of this material frequently have visions of greater profits by converting this cement copper into electrolytic cathodes, casting copper, blue vitriol, or some other more profitable forms. The eventual treatment of this class of material, when in sufficient quantity, will be simple melting or fusion in a coal- or oil-fired reverberatory and, perhaps, then tapping molten copper into a refining furnace and subsequently refining so as to produce a casting copper or anodes for the electrolytic refinery. Such an operation would not require a large expenditure.

The advantages of electrolytic copper in the making of alloys and bearing metals is more and more appreciated, and the market for casting copper is irregular and fluctuating, with the result that direct uses for secondary coppers are becoming less, thus reducing the field for casting copper. In all probability, the most economical disposal of this material will be smelting and casting into anodes and shipment to a refinery.

Hydrogen Sulphide.—Hydrogen sulphide may be considered the next best precipitant for copper from leaching solutions. If hydrogen sulphide is applied to a copper sulphate or copper chloride solution, copper is precipitated as cupric sulphide and acid is regenerated equal to that combined with the copper. This regenerated acid may be used to dissolve further copper.

Hydrogen sulphide may be generated in various ways, the cheapest probably being by the action of sulphuric acid on a low-grade copper matte. Tests made with hydrogen sulphide generated from sulphuric acid and low-grade matte have given the costs of precipitation to be equivalent to iron at $20 per ton, or about 1 cent per pound of copper.

Greenawalt recommends hydrogen sulphide for the precipitation of copper from discard solutions. There are no leaching plants known to be in operation at this time where this gas is used as the precipitant of the copper from solutions.

Sulphur Dioxide.—The most interesting process that has been developed for copper precipitation is that of George D. Van Arsdale[28], who found that, when a solution containing copper and ferrous sulphate is saturated with sulphur dioxide and is then heated under pressure, a reaction occurs resulting in the precipitation of about half of the copper as finely divided metallic copper together with the formation of free sulphuric acid. This process has been tried at several plants, and it was found that between 60 and 70 per cent of the copper could be quite economically precipitated. The principal difficulty was how to recover the remainder.

Commercial Leaching Installations.—The most important copper-leaching plants that have been constructed are briefly described below.

The Chile Copper Co.—The ore treated by the Chile Copper Co. at Chuquicamata, Chile, consists of oxidized minerals in seams and fissures affording simple and rapid extraction. The ore contains among other minerals the unusual basic copper sulphate or brochantite. The mineral is readily soluble in dilute sulphuric

acid and introduces copper sulphate into the solution, which, on electrolysis, liberates free acid. The mineral is reported frequently to be present in sufficient quantity to make the addition of acid from outside sources unnecessary.

The ore, averaging about 1.7 per cent copper, is mined with steam shovels, loaded on cars, and transported by rail to the crushers. Successive crushing operations reduce the steam-shovel size so that 30 to 90 per cent will pass 0.371-in. mesh. The plant has a capacity of over 1,400,000 tons per month.

Belt conveyers deliver the crushed ore to a traveling bridge, from which it is discharged into one of six reinforced-concrete tanks lined with asphalt, 150 ft. long by 110 ft. wide by 16½ to 18 ft. deep, set end to end and holding about 11,500 tons each. The ore is charged into one end of the tank until the top of the tank is reached, and the bridge is then advanced as such a rate as to keep the level constant. This method of charging a tank classifies the ore so that the coarsest material will be at the bottom and the finest on top.

The ore may be loaded into the tanks either into solution or into a dry vat, depending on whether or not solution is available. It is allowed to soak for 8 to 24 hr. before the first strong solution is run in. A second soaking period of 24 to 72 hr. ensues, after which a second strong solution is applied at the top. Three more strong leaches are given and then six successive washings with liquors of decreasing copper content.

A certain quantity of each solution coming from the ore is removed for the complete deposition of the copper, in order to take care of the impurities and to compensate for the introduction of wash water to the system. The impurities at Chuquicamata consist principally of the sulphates of magnesium, sodium, and potassium, together with a small quantity of nitrate and chloride. The former, while not detrimental to the operation, would accumulate to such a point as to render the solution inactive. The chlorides and nitrates go into solution with the copper and must be eliminated as far as possible. The chlorides are removed by agitating the pregnant solution in the presence of metallic copper, whereby the chlorine will be precipitated as a more or less insoluble cuprous chloride. About 85 per cent of the chlorine is removed in this manner, and about 1 ton of solution is dechlorinated per ton of ore treated. The nitric acid is eliminated by the use of a little sulphur dioxide, which is converted to sulphuric acid. Both chlorides and nitrates when present in appreciable quantities prevent the use of lead anodes.

The ore is ideal for leaching, the extraction obtained averaging consistently over 90 per cent. It has been said that each ton of ore contains between 20 and 30 lb. of what might be called latent acid.

The pregnant solution after dechloridizing is sent to the electrolytic tank house for precipitation[30]. These tanks are of reinforced concrete. There are 1098 cells in operation. Lead anodes were at first tried in the experimental plant but were not found satisfactory. A German anode made of fused magnetite was then used. The war (First World War) with Germany made these difficult to obtain, and a ferrosilicon alloy was substituted. Later these were replaced by copper-silicon and antimonial lead anodes developed by the research department of this company.

Power for all operations is generated at a plant built on the coast, some 150 miles from the mines. Of the total power generated, a little over 80 per cent is used for copper deposition. About 0.85 lb. of copper is deposited per kilowatt-hour to the tank house. Refining furnaces have been provided, and the cathodes are melted and cast into commercial shapes at the plant, the product leaving Chuquicamata as the highest grade of electrolytic copper.

This process is being successfully applied to some four or five million tons per year, turning out at practically one continuous operation some 180,000,000 lb. of refined copper from an ore that could not be treated by any other known method.

New Cornelia Copper Co.—About the time that the Chuquicamata plant of the Chile Copper Co. was ready to begin operations, the details of the process to be used in treating the ores of the New Cornelia Copper Co. at Ajo, Ariz., had been practically decided upon.

The problem in Ajo differed from that in Chile in that the ore to be treated (1) was of a lower grade; (2) did not carry any latent acid compounds, such as basic copper sulphate; (3) was less readily soluble. On the other hand, the problem at Ajo was simpler. There were neither chlorides nor nitrates to contend with in the ore. Tests could be carried out on a larger scale and closer to the scene of actual operations; supplies were less expensive and more easily secured.

After a period covering nearly three and a half years and during which some 15,000 tons of ore were treated, a process was developed, the results of which could be positively foretold, and by which the deposit was successfully worked out.

The process adopted was as follows: (1) mining by steam shovels, the maximum size to be controlled by the size of a fragment that will pass the shovel dipper; (2) transportation of the ores in cars that will stand up to the rough service and discharge freely any fragments that passed through the dipper of the steam shovel; (3) the delivery of the ore, without any storage other than cars, directly into a crusher that will receive any fragment discharged by the car; (4) crushing of steam-shovel size to as near ¼ in. as practicable; (5) leaching the crushed ore 8 days by a countercurrent system and upward circulation, using sulphuric acid and such ferric sulphate as is inherent in the process; (6) reduction by sulphur dioxide gas of the ferric iron remaining in the neutral solutions from the leaching tanks; (7) the electrolytic deposition of part of the copper from this reduced solution, which is then returned to the leaching solution; (8) the continuous discharge of such portion of the neutral solution as is necessary to prevent accumulation of sulphates other than copper to the saturation point; (9) the recovery of the copper content of such discarded solution as cement copper precipitated on iron; (10) the treatment of a part of this cement copper with solution from the electrolytic tank house to the end that the copper be returned to the circulation and a part of ferric sulphate reduced.

Crushing.—The ore was mined by steam shovels and was loaded and delivered to the crushing plant in side-dump cars. The crushing plant was divided into two departments, coarse and fine, which were separated by a 10,000-ton storage bin.

The 10,000-ton storage bin between the coarse and fine crushers was of steel, built on an elevated reinforced-concrete platform. The ore was drawn from it automatically onto a set of five belt conveyers, equipped with magnetic head pulleys, which delivered the ore to five units of Symons vertical-shaft disk crushers. Each unit consisted of three interchangeable crushers. The first was set to crush to inch cubes. The crushed material was elevated and screened; the undersize by-passed the remaining two crushers, which were set in parallel. The oversize passed to these two crushers, which were set to crush to the desired size. The entire product was fed to a system of belt conveyers, which led through a sampling plant to the leaching vats, which furnished the only storage for the crushed ore.

Leaching.—The leaching tanks, 88 ft. square and 17 ft. 4 in. deep inside, were built of reinforced concrete with wooden bottoms. Each had a capacity of 5000 tons of crushed ore. The sides and the launders of the tanks were lined with 8-lb. lead and the bottom with 6-lb. 4 per cent antimonial lead. The filter bottom was laid over the lead bottom and consisted of 5 × 12 in. joists on edge laid on 16-in. centers, covered with 2-in. shiplap planks that were bored with ⅜-in. holes on 2-in. centers countersunk from below. Under the center of the filter bottom, and at right angles to the wooden floor joists, a distributing launder was set in the floor, through which the solution enters and from which it is distributed under the filter bottom.

The lead lining on the sides of the tanks was protected from abrasion by a covering of 2-in. planks. At the top and sides of each leaching tank were two overflow launders extending the length of the tank, one end being connected with the suction of a circulating pump. The charging was done by a machine especially designed for this plant and known as the spreader bridge. It consists of a traveling bridge of structural steel which spanned the tanks and traveled, as desired, lengthwise with the row. The bridge supported a belt conveyer, which received the crushed ore from the belt on a central structure. A tripper on this belt spread the ore in the leaching tanks.

The tanks were charged by filling to the top of the tank at one side, allowing the ore to assume its natural slope, or about 45 deg., and then continuing at one side and discharging the ore at the top of the slope, allowing the coarser material to run to the bottom and the finer to remain somewhat higher up, thus giving a rough classification. The bridge is moved slowly forward as the filling of the tank progresses. This plan was suggested by the engineers of the Chile Copper Co., who have obtained the best results through this method of filling.

The crushed ore was leached for 6 to 8 days by a countercurrent system and upward percolation, using dilute sulphuric acid as the principal solvent.

The solution in each tank was circulated by two 15-in. vertical centrifugal pumps having a capacity of 3500 gal. per min. each. These were driven by direct-connected 40-hp. vertical motors. The head against which the pumps work was equivalent to the friction head of the solution passing through the ore. The discharge from one of these pumps was provided with a by-pass which permitted a portion of the solution to be advanced to the next tank. Both pumps were throttled to give a circulation of about 4000 to 5000 gal. per min. through the ore. Of this amount about 1000 gal., called the solution advance, was continuously passing through from tank to tank. The high-acid solution, which has averaged about 2.5 per cent free acid for an 8-day leach, coming from either or both the tank house and the solution storage, and going on the oldest ore, was called the "acid advance." The nearly neutral solution coming off the newest charge and going to the reduction towers was known as the "neutral advance."

Upon the entrance of a new charge into the circuit the solution remaining in the oldest tank was drained to the solution storage, where it was standardized with acid and later used as acid advance. After thorough draining, the tank was ready for the wash water.

As the copper entrained in a charge after leaching was about one third of the total copper dissolved, the question of thorough washing was very important. Four successive wash waters with drainings were used.

The fourth wash of any one charge was used as the third wash of the succeeding charge, the third used as the second, and the second as the first. In other words, each wash water was used four times, the copper contents increasing each time, when it was incorporated into the system to make up the continuous losses of solution. These losses were due to evaporation, discard, and solution entrained in tailings.

After a charge had been washed and drained, the tailings were removed from the tank by a Hulett unloader, similar to unloaders used on the Great Lakes for unloading iron ore from boats. A heavy steel bridge on trucks spanned the leaching tanks and traveled their entire length. On this bridge traveled a trolley carrying a walking beam, bucket leg, and bucket of 12-ton capacity. The unloader had a rated capacity of 500 tons per hr. and generally excavated a tank of tailings in 10 to 11 hr.

Reduction of Iron.—In the electrodeposition of copper from a sulphuric acid solution, iron, if present, will consume electric energy, by its alternate oxidation and reduction, thereby reducing the quantity of copper deposited per unit of current. During the experimental work, the control of the ferric iron proved one of the hardest

problems to solve. A patent diaphragm anode was tried and gave good results, but was cumbersome and difficult to keep in order. Later, tests made on a process in which iron and alumina were precipitated as hydrated oxides by the addition of roasted copper ores gave good results, but the method was considered too complicated for an ore of this character. The idea was then suggested of using the natural oxides and carbonates in the ore itself as the precipitant of the ferric sulphate; in other words, the precipitation of the principal impurities in the solutions upon the charge itself. Early tests made on a small scale were very promising, but tests carried out later on a larger scale failed to give the desired results. For the first 15 or 20 days, the copper in the newest charge of ore was sufficient to precipitate all the ferric iron that was contained in the solution passing through the ore. However, as the acid concentration on each charge increased, the precipitated ferric iron was redissolved and eventually accumulated to such an extent that the iron in the solution was in excess of the copper available as a precipitant.

It was now decided to resort to SO_2 reduction. The general opinion was that this was both unsatisfactory and difficult. This proved to be the case in solutions decidedly acid, but where neutral or slightly acid solutions were used, reduction proved quite easy. For these tests elemental sulphur was used, as it was believed that a gas with the maximum percentage of SO_2 was most essential and that a rich gas could be produced only by burning elemental sulphur.

In the sulphite-pulp industry large quantities of sulphur gas are produced and absorbed, and, accordingly, the method of producing and absorbing the gas used in that industry was investigated. It was found that at some plants pyrites were used and that under proper conditions a gas of 12 per cent SO_2 could be produced. The only objection in the sulphite-pulp industry to the use of pyrites was the tendency of small calcined particles to be carried into the solution and thence into the pulp. Upon investigation it was decided to make use of the cheap and abundant supply of the high-sulphur low-copper ores of the Bisbee district.

A bucket elevator and a conveyer equipped with automatic tripper delivered the crushed ore to hoppers situated above four Wedge roasters. These roasters were 22 ft. 6 in. in diameter, had seven hearths, and were belt-driven by 7½-hp. motors.

The gas leaving the roasters entered a spray or cooling chamber. This chamber was 14 ft. square, 94 ft. long, and was built of 8-lb. lead supported on a wooden framework. Nozzles were distributed over the top and sides through which "neutral advance" was sprayed to cool the gas before it entered the towers. Between 90 and 100 gal. of solution per minute was required to supply these sprays. The ferric iron in the solution used in cooling the gas was practically all reduced and the solution joined that coming from the towers. The temperature of the gas in its passage through the spray chamber was reduced from 600 to 150°F. A flue connected the spray chamber with the bottom of the first pair of towers, dividing the gas equally between them.

There were six towers arranged in pairs. Two pairs of the towers were part of the original equipment and were 40 ft. high and 20 ft. in diameter. These were built of sheet lead, supported on a steel framework. The other pair were 28 ft. in diameter, 40 ft. high, and were built of ordinary redwood tank construction, hooped together with iron rods. As an additional precaution against gas leakage, the wooden towers were painted with asphalt and covered with roofing paper under the hoops. The towers rested upon a reinforced-concrete base, provided with a lead pan. All towers were filled with boards placed on edge, the width of a board apart, and in layers. Each layer was laid at right angles to the one immediately below it. The solution was distributed over the top of the towers by a system of launders provided with gas seals. Between the second and third pairs of towers was a fan which drew the gas from the

roasters through the spray chamber and a third set of towers, and forced it through the second and first sets to the atmosphere. The temperature of the escaping gas was that of the atmosphere.

The solution (or neutral advance) to be reduced traveled countercurrent to the flow of gas, *i.e.*, the most reduced solution came in contact with the strongest gas. The solution coming from the newest tank of ore was pumped to the top of the third pair of towers by a centrifugal pump. The solution distributed by launders and gas seals flowed down over the filling, thus coming into intimate contact with the rising gas. At the bottom of each pair of towers there was a concrete lead-lined sump, into which the solution flowed and was then pumped through the next pair of towers. From the first pair of towers the solution was pumped to the second pair, then to the third pair, and then to the so-called settling tank, whence it went to the tank house. The purpose of this settling tank was twofold: (1) to settle out the slime, (2) to get the benefit of the additional reduction that was found to take place in a neutral or slightly acid solution on standing.

Electrolytic Deposition.—The electrolytic tanks were housed in a structural-steel building, 166 ft. wide and 280 ft. long, having sides only partly enclosed to give good ventilation. The tanks were all on the same level, none in cascade.

The cellar, which was open on all sides, had an asphalt floor draining to gutters that led to a sump at each end of the building. There was headroom throughout the cellar to permit regular inspection of tanks, piping, and feed wires.

The electrolytic tanks were arranged in banks with aisles between. There were 12 banks of 10 tanks each and 4 banks of 8 tanks each, making a total of 152 tanks. Each tank was separated from the adjacent tank by a 3-in. air space. All tanks were made of Oregon pine, lined with 7-lb. chemical lead. The inside dimensions of the tanks were 29 ft. 7 in. long, 4 ft. 9 in. wide, and 4 ft. 3 in. deep. These tanks were supported on concrete columns and were insulated by tile blocks covered with sheet-lead caps. Each tank was provided with a 4-in. clean-out plug. There were also two perforated lead diaphragms, one at each end of the tanks, to assure a uniform circulation. The inlet to each tank was fitted with a 3½-in. diaphragm valve and a 3½-in. glazed stoneware gooseneck for insulating purposes. At the outlet end there was a lead overflow pan fitted with a 4-in. tile pipe suspended in a 10-in. lead boot connected to the discharge pipe.

Each tank had 84 anodes, making a total of 12,768 in the tank house. The anodes were of lead containing 3.5 per cent antimony, of an average weight of 215 lb. They were 40 × 51 × ¼ in. thick and were suspended by two ¼ × 1¼-in. copper bars secured to the tops of the anodes. The submerged surface of all anodes was 41 × 41 in. The spacing of anodes was 4½ in. on centers. The distance from the bottom of an anode to the bottom of the tank was 8 in., while that of the cathode was 7 in. Short circuits were prevented to some extent by providing the anodes with eight chemical glazed-porcelain insulators distributed over the anode faces.

Much doubt was expressed about the life of the lead anode, and some very positive statements were made regarding their probable length of life. Continuous service failed to show appreciable oxidation, except after years of service.

There were 77 cathodes to a tank, or 9779 cathodes in the tank house, exclusive of starting-sheet blanks. The cathodes, 42 in. square, were totally submerged. They were suspended upon copper bars by loops made from starting sheets. The original starting sheets weighed about 15 to 18 lb., while the finished cathodes weighed 130 to 140 lb.

The cathodes produced varied from 99.15 to 99.85 per cent in copper content, the impurities being principally slimes, held by mechanical entanglement. The greater the density of the electrolyte, the lower was the copper content in the cathodes

and the greater the insoluble matter, iron, and alumina. The cathodes always contained more or less chlorine, varying from 0.05 to 0.35 per cent. There being no arsenic or antimony in the ore, and little in the acid, the average arsenic content of the cathodes was less than 0.0015 and the antimony less than 0.0005 per cent.

Twenty-five tanks operated on starting sheets, each tank containing 77 starting blanks, or a total of 1925 blanks. The starting blanks were of rolled 3.5 per cent antimonial lead, 53 × 43 × ¼ in., and were large enough to allow a small amount of trimming, which was done with a squaring shear. The anodes in these tanks were 3.5 per cent antimonial lead, and were 41 × 52 × ¼ in. They did not have porcelain insulators, as these tend to spot the starting sheets. The spacing of anodes in these tanks was the same as in the commercial tanks. The tank construction and other details were likewise similar.

The electrodes hung parallel to the flow of solution (or parallel to the length of the tanks) to give a free circulation of the electrolyte. Alternate bus bars extending across the tanks connected the electrodes in parallel and the tanks in series. These bus bars, placed across the tank, divided it into seven sections or cells. The intermediate bus bars were 1½ in. wide and 4 in. deep, while the end bus bars were 1 in. wide and 4 in. deep. Soldered along the top of each bus bar was a triangular piece of copper, ½ in. high, giving a point contact to the electrode bars. Small maple blocks impregnated with linseed oil insulated cathodes and anodes from opposite bus bars. These bus bars were supported on insulated iron castings, which, in turn. rested on the tank cleats. The maximum current density was 8 amp. per sq. ft. of cathode surface when operating under normal conditions. With an average current efficiency of 80 per cent, this meant a daily gain of about 10.25 lb. per cathode, or a total capacity of 120,000 lb. of electrolytic copper per day. The drop of potential between anodes and cathodes averaged close to 2.00 volts. There was a tendency for the voltage to drop during the summer owing to an increase in the temperature of the electrolyte.

The solution flow in the tank house was part of a closed circuit with the leaching and reduction plant, receiving a continuous flow of solution from them. This flow, coming always off the newest ore, then through the towers and settler, was regulated by means of weirs and varied from 800 to 1500 gal. per min., depending on operating conditions. This volume was divided among the 16 banks of tanks, those on starting sheets getting generally a little more than those on cathodes. By this arrangement each bank of tanks on cathode received between 60 and 70 gal. per min. of reduced solution. Each bank unit consisted of either eight or ten tanks, a sump, and a 9-in. vertical-type centrifugal pump having a capacity of 1600 gal. per min. Each bank had an individual circulation of 1600 gal. per min. between it and the sump, while an overflow arrangement provided for the return of such a portion of the electrolyte as was equivalent to reduced solution added.

The current efficiency depended on the quantity of ferric sulphate present, owing to the reaction between ferric sulphate and metallic copper. The ferric iron content in the solution was kept as low as possible. With the total iron not over 2 per cent, the ferric iron in the electrolyte probably did not exceed 0.5 per cent.

At the beginning of operations in the tank house, a great deal of difficulty was encountered by the dropping of cathodes in the electrolytic tanks, due principally to the corrosive action of the ferric sulphate on the loops at the solution level and on that part of the cathode covered by the ends of the loops. Corrosion at the solution line was easily remedied by raising and lowering the solution level in the electrolytic tanks, but the corrosion of the cathode sheet between the loop ends was far more difficult to overcome. Later this condition became worse with the increase in the ferric iron and higher temperature of the electrolyte. The dropping of cathodes not

only caused bad short circuits in the tanks, but also made it necessary, when pulling cathodes for shipment, to pull individual sheets with tongs, which made it almost impossible to handle the daily output of cathodes. Considerable damage was also done to the lead lining of the tanks, and the danger from accidents was more than usual. Numerous schemes to overcome this difficulty were suggested and tried, until it was found that, by splitting the ends of the loop and attaching them with a Morrow machine in such a manner that the portion of the starting sheet adjacent to the loop was exposed to the deposition of copper, not only the loop, but also the sheet built up, making a good firm joint. After the adoption of this method, no further trouble was experienced with dropping sheets.

As previously mentioned, only about 45 to 50 per cent of the total acid used in an 8-day leach is utilized in dissolving copper. The remainder is used in dissolving impurities. If copper only is removed from the solution, the other substances will gradually accumulate and the solution will reach a condition where it will become sluggish in dissolving the copper from the ore. To keep the solution active, it is evident that a portion must be discarded and replaced with fresh water. The quantity of solution discarded per day must contain impurities equivalent to the amount dissolved per day, if the accumulation is to be avoided. In the experimental work it was found that, under similar conditions, nearly all the substances that went into the solution were present in a fairly constant ratio to one another. Of the various impurities dissolved, iron is the most easily and quickly determined and was used as the indication of the quantity of solution necessary to be discarded. The experimental work clearly demonstrated that the best results were obtained when the total iron in the solution did not exceed 2 per cent.

The original cementing equipment consisted of six sections of reinforced-concrete launders. These were arranged in two parallel rows of three sections each. The bottom of each launder sloped toward three side clean-out gates. The scrap iron rested upon a grated wood floor. The solution flowed through each one successively, but could be by-passed to allow the cleansing and refilling of any of the sections. From these launders the waste solution went to the desert.

Under good operating conditions practically all the copper was precipitated. When a launder was no longer efficient, the solution to that launder was by-passed and the solution remaining in it was drained. The cement copper was shoveled out onto wooden grates, where the iron was washed off with a hose, and the unconsumed iron was returned to the launders.

Cement copper when clean and finely divided dissolves readily in ferric sulphate, with the formation of copper and ferrous sulphates. By so doing not only is the cement copper dissolved, but the ferric iron is reduced also. The plan was to hose off the loosely adherent copper from the scrap iron to the bottom of the tank and then flush it into one or more circular lead-lined tanks, called agitators. These tanks are 20 ft. in diameter and 6 ft. deep, provided with a stirring device, driven by a small motor; 125 gal. per min. of tank-house return solution can be circulated through each tank.

This plan of redissolving the cement copper was carried out when the operating conditions of the plant required it. The principal objections to the continuous use of such a plant are that by redissolving the cement copper in tank-house solution the total copper output of the plant is reduced, which at times does not give the greatest profit possible. Although the Ajo plant is history, this lengthy description is given as it details the operation of a plant, the details of which were carefully planned, and which functioned profitably to the exhaustion of the deposit.

Union Minière du Haut Katanga.—Sulphuric acid leaching was practiced for a time on the shale ores of the Union Minière du Haut Katanga. The plant presented

some novelties as compared with other installations, in that continuous and not batch leaching was employed; the leaching was by agitation instead of percolation; washing the sand tailings was carried on in multideck Dorr classifiers arranged countercurrent; washing the slime tailings was performed continuously in thickeners; the iron and alumina in the solutions were held within reasonable limits by continuous purification through neutralization of a part of the solution with original ore or concentrates[36].

Some condition was present, which has never been satisfactorily explained, that quickly ate away any copper alloys, and only lead, duriron, some of the chrome-nickel irons, rubber, asphalt mastic, glass, and porcelain could safely be used in contact with the solutions. This was possibly due to cobalt.

The removal of iron and alumina by precipitation with a portion of the ore was the first successful application of this idea to commercial practice. A portion of the solution was constantly withdrawn and agitated for 17 hr. with raw ore or concentrates, completely neutralizing it. The pulp was then classified, the sands were sent back to the leaching circuit, and the slime was sent to a thickening-washing circuit which was always maintained at neutrality. The washed slime discarded from this operation ran about 1 per cent Cu, but apparently it was figured that control of the iron and alumina was worth this price.

Andes Copper Co.—The leaching plant of the Andes Copper Co. at Potrerillos, Chile, is a sulphuric acid leaching operation, a 6-day countercurrent leaching followed by a 1-day countercurrent wash. The operation is unique in that through a complete neutralizing with 200-mesh limestone the entire leach solution is purified from iron, alumina, arsenic, and phosphorus before it goes to the tank house. This means that all the free acid in the leach solution and that combined with the iron and alumina is thrown down as calcium sulphate and is eliminated along with these impurities. This consequently means that about 63 lb. of 60° sulphuric acid is required per ton of ore treated. This acid is produced by treating a part of the gases from the roasting plant for the production of sulphuric acid[38].

The first leach of the ore is by upward percolation, but the succeeding five leaches are by downward percolation. The tanks are concrete with mastic floors and acid-proof brick walls. The filter bottoms are of the Inspiration type.

It was found necessary to remove the slimes which run approximately 5½ per cent and to treat them by agitation. Any discard and excess wash solutions are treated with crushed limestone by agitation at about 37°C. The precipitated copper carbonate and the accompanying calcium sulphate are fed back into the purifiers, the copper carbonate acting in the same way as does the limestone to neutralize acid and throw down iron and aluminum.

Chlorine is eliminated by agitating the purified leach liquor with excess of cement copper, which throws down much of the chlorine as cuprous chloride. The settled residue consisting of cuprous chloride and cement copper is treated with ferrous-chloride solution, which dissolves the cuprous chloride. The copper in this solution is precipitated with scrap iron, washed, and used for further dechloridizing. The copper is then precipitated from the dechloridized solution by electrolysis, using 15 per cent antimonial lead anodes. The copper is reduced to about 11 g. per l. in the tank house, the spent electrolyte going back to the leaching tanks.

Inspiration Consolidated Copper Co.—The Inspiration Consolidated Copper Co. in October, 1926, commenced large-scale leaching of an ore carrying oxidized copper and chalcocite by the use of ferric sulphate and sulphuric acid. After 2 years a flow sheet was adopted in which slime was removed, treated first by flotation, then by agitation, while the sands were treated by upward percolation. The lixiviant was regenerated by electrolytic precipitation. The solution from the tank house carried about 9 g. per l. of iron, 41.1 g. of acid, 21.6 of copper (in 1931); the ferric iron in the

solution from the leaching tanks ran 2.8 g. per l., but by the time it went to the tank house it carried 4.0 g. of ferric iron (total iron, 20 g.). The solution to the tank house carried 26.4 g. of copper (1931). The anodes are 8 per cent antimonial lead. Starting sheets for the tank house are made in a small section of the tank house using anodes cast at the Inspiration smeltery, near by. It was found highly advantageous to warm the solutions so that they went on the ore at 42°C. Wash waters or waste solutions were treated with detinned scrap before discarding[37].

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CHAPTER XIII

ELECTROLYTIC REFINING OF LEAD

By Gustave Reinberg[1]

History.[2]—Commercial electrolytic refining of lead dates from the development of the fluosilicate electrolyte by Anson G. Betts, at the beginning of the twentieth century. Earlier experimenters had endeavored to use acetate or nitrate solutions, from which the lead was deposited at the cathode in the form of loose crystals or sponge, which fell to the bottom of the tanks or was removed by mechanical scrapers. The practical difficulties of this method of operation, especially those incident to the washing and melting of the refined lead, proved insurmountable. Betts[1] investigated a number of complex acids, including fluosilicic, fluoboric, dithionic, methyl and ethyl sulphuric, and several sulphonic acids, all of which formed very soluble lead salts and produced electrolytes of high conductivity. He found that by the addition of an organic colloid, such as glue or gelatin, these electrolytes could be made to produce a solid and adherent cathode deposit, with a density equal to that of cast lead. Considerations of cost and stability have made fluosilicate electrolytes the logical choice for refining operations, although fluoborates and sulphonates have had a limited application for special purposes such as electroplating.

The pioneer Betts process refinery, that of the Consolidated Smelting & Refining Co., Ltd., at Trail, B. C.[2] has been in continuous operation since 1903, and has been successively modernized and enlarged to a capacity in excess of 500 tons per day. The plant of the U. S. Smelting Lead Refinery Inc., at East Chicago, Ind., started operations in 1906 and has also been extensively modernized in recent years. The latest Betts refinery to be built is that of the Cerro de Pasco Copper Corp., at La Oroya, Peru, the first unit of which was started in 1934, followed by a large capacity enlargement in 1937. This plant was specially designed for the treatment of very impure bullion, and its operating conditions differ in several respects from previous practice[3].

The Betts process is notable for its ability to produce refined lead of exceptional purity, and is particularly adapted to the treatment of bullion containing bismuth, or in which the total content of impurities is large. It does not offer any significant metallurgical advantage over the older Parkes process for the refining of relatively pure bismuth-free bullion such as that produced from Missouri ores, but may have an economic advantage if fuel cost is high in comparison with electric-power rates.

Electrochemical Data.—As lead is divalent in fluosilicate solutions, the electrochemical equivalent is 3.865 g. per amp.-hr., or 0.2045 lb. per amp.-day. A current efficiency of 90 to 95 per cent of this figure is usually realized. The most economical current density will normally be between 15 and 18 amp. per sq. ft. The electrolyte composition may vary considerably, representative values being 80 g. per l. each of Pb and free H_2SiF_6, corresponding to a total SiF_6 content of 135 g. per l. Electrolyte resistance varies with composition as shown in the attached curves (Figs. 1 and 2). This resistance also varies with temperature in the usual manner (Fig. 3). In tem-

[1] Metallurgical engineer, Cerro De Pasco Copper Corp., New York.

[2] References in this chapter are to similarly numbered references in the Bibliography at the close of the chapter.

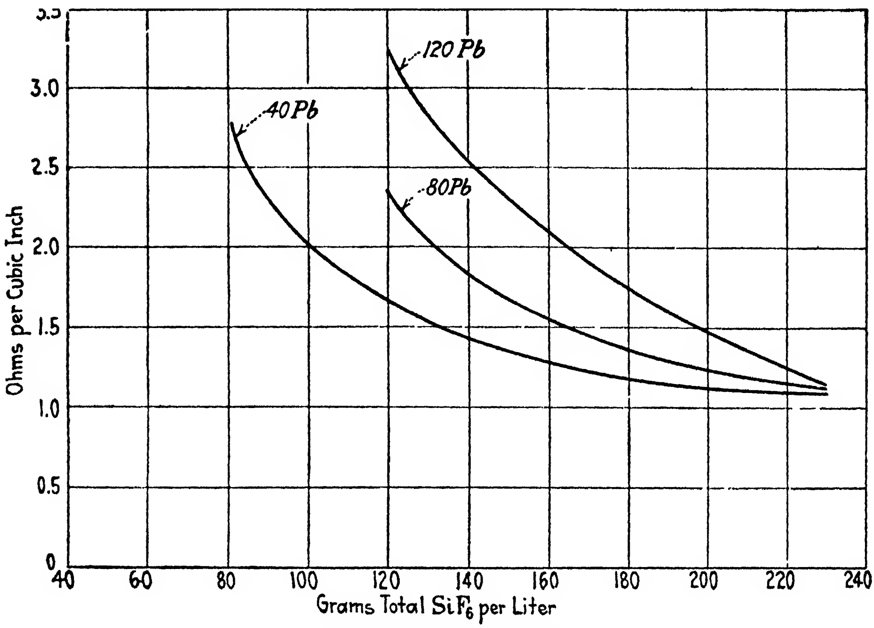

FIG. 1.— Electrolyte resistance curves.

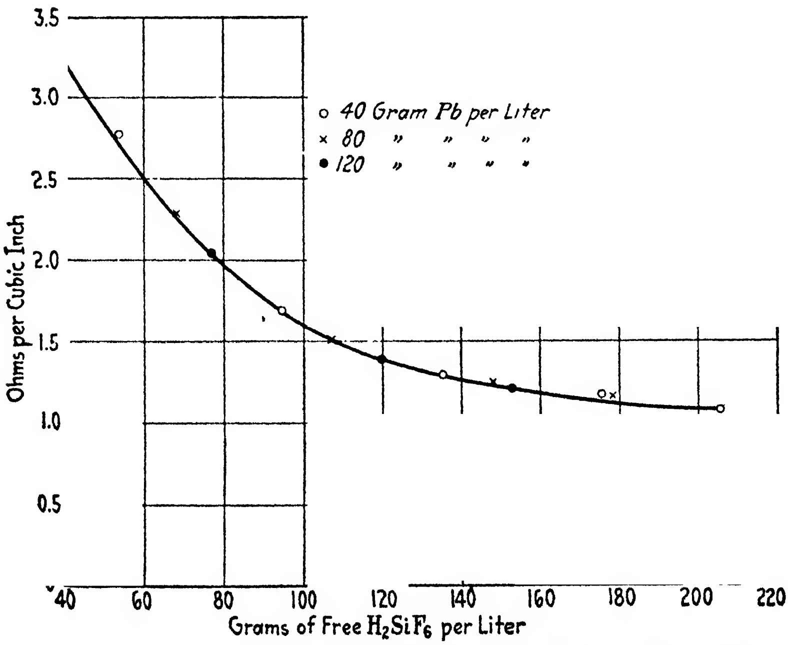

FIG. 2.—Ohms per cubic inch of electrolyte, varying the free H_2SiF_6 with 40, 60 and 80 g. of lead per liter.

perate climates, an equilibrium temperature will ordinarily be reached at some permissible value between 30 and 40°C., but in extremes of weather, some artificial heating or cooling may be required, since very low temperature would increase resistance unduly, and excessively high values might damage tank linings. Under these conditions of current density, electrolyte concentration, and temperatures, the average volts per cell will approximate 0.45, and the direct-current power consumed in the cell circuit will be about 120 kw.-hr. per ton.

Cell circuits have generally been designed for a total current of 4000 to 6000 amp. direct current. The over-all voltage of a 4500-amp. circuit is approximately equal, numerically, to its refining capacity in short tons of lead per day.

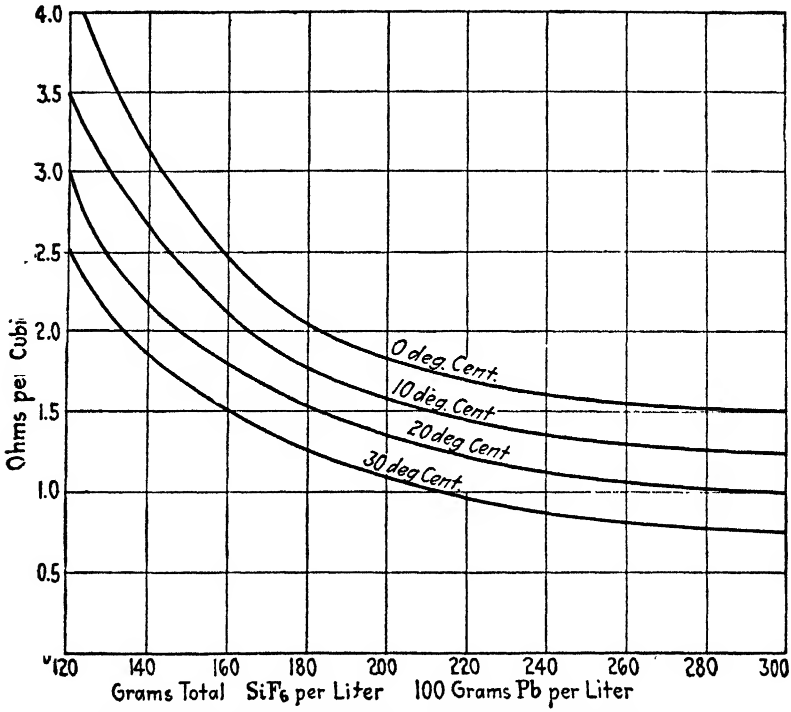

FIG. 3.—Temperature-resistance curves, fluosilicate electrolyte.

The amount of glue used as an addition agent ranges from 0.5 to 1.5 lb. per ton of lead produced. It has been found that bindarene flour (a by-product of the paper-pulp industry) may be substituted for half or two-thirds of the total glue used, the glue-bindarene mixture often producing a better deposit than can be obtained with glue alone. The addition agents are, for the most part, deposited with the lead and produce a characteristic odor when the cathodes are melted.

The metals having electromotive-solution potentials higher than lead, *i.e.*, Zn, Cd, Fe, Ni, and Co, are normally absent from lead bullion, or are present in such small amounts that no injurious accumulation in the electrolyte will occur. An electrolyte can therefore be used for many years without purification. Small accumulations of iron, alkali metals, and nitrogenous decomposition products of glue are found in old electrolytes, but usually have no harmful effect on the operation.

Tin presents a special case, in that its electrolytic solution potential is nearly identical with that of lead. It may therefore be dissolved and deposited with lead at the

cathode, if present in the anodes being refined. Tin which thus contaminates the cathodes is removed by mechanical drossing or blowing with air when the cathodes are melted. In general, a portion of any tin present in anodes will form intermetallic compounds with other impurities present, which lower its solution potential and cause it to be retained in the anode slime. If the bullion under treatment contains sufficient tin to warrant the recovery of this element, it may therefore be expedient to remove it by a high-temperature drossing operation[4] before casting the bullion into anodes, rather than to recover it from slimes and cathode dross. The codeposition of tin and lead from fluosilicate solution is employed as a commercial method for the production of solder[5].

It has been observed that thallium is another element with anomalous behavior, which may be only incompletely removed from lead by electrolysis. Thallium, however, will occur in lead bullion only under exceptional circumstances, even when the parent ores contain it, as it is practically completely eliminated from the lead blast furnace by volatilization.

The impurities ordinarily associated with lead, all of which have lower solution potentials than lead and remain undissolved at the anode during electrolysis, are As, Sb, Bi, Cu, Ag, Au, and Te. These impurities, if present in sufficient amount, form a highly porous layer or blanket of slime which remains attached to the face of the anode and retains the original shape and appearance thereof as the lead is dissolved. The solution filling the pores of the slime blanket, a volume which is of course equal to that of the lead that has been removed, is not by any means of the same composition as the freely circulating electrolyte. It consists, rather, of a nearly neutral solution of lead fluosilicate of high concentration. The voltage drop that appears across the slime blanket, which increases as corrosion of the anode proceeds, is produced by the ohmic resistance of the solution in the pore volume and by "concentration-cell" effect.

In modern practice, the working life of the anode is determined by the nature and amount of impurities present in the bullion treated. In this way the thickness attained by the slime blanket is limited to a value such that the maximum voltage drop across it is less than the electrolytic potential difference available for impurity separation, by a safe margin. For usual types of bullion and normal current densities, appropriate anode corrosion periods will range from 2-day anodes for bullion containing 90 per cent Pb or less to 6-day anodes for bullion containing 98 per cent Pb or more; the exact limits must in every case be established by trial. This technique has eliminated the difficulties encountered in earlier years, when heavy anodes with 8- or 10-day corrosion periods were universally employed. With these long corrosion periods, voltage drops were excessive unless the bullion treated was very pure, and with very pure bullion, the slime blanket was too soft to be thoroughly adherent. In either case, the purity of the lead produced was adversely affected. The minimum amount of impurity that will produce a slime of satisfactory physical characteristics is dependent on the chemical composition of the slimes as well as other factors. This point requires careful attention if the bullion contains over 97 per cent Pb, and in certain cases, impurities may have to be recirculated to maintain proper conditions.

It is preferable to limit the maximum life of the cathodes to a 4-day period. Five- or six-day cathodes have been occasionally employed, but the increased weight and roughness of the deposit are serious handicaps. To facilitate cell-changing operations, the cathode life should be a factor or a multiple of the anode life, therefore 3-day cathodes would be used with 3- or 6-day anodes and 4-day cathodes with 2- or 4-day anodes.

Manufacture of Electrolyte.—Fluosilicic acid, H_2SiF_6, which is also known as hydrofluosilicic acid, is obtained as a by-product in the manufacture of superphosphate

fertilizer; it may also be prepared by dissolving finely ground silica in hydrofluoric acid of about 40 per cent strength. Either percolation towers or agitator tanks may

FIG. 4.—Night view of Betts tank house; dip washing tanks for corroded anodes in foreground.

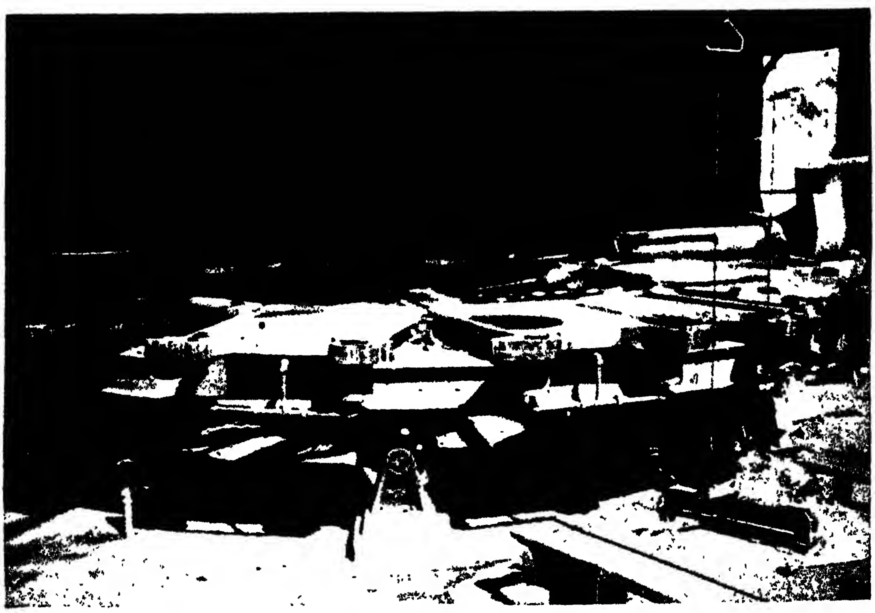

FIG. 5.—Anode-casting wheel with meter type of pouring device.

be employed for this purpose. An excess of silica must be used and the operation finished at an elevated temperature to secure complete conversion. The hydrofluoric

acid is produced by distillation from a mixture of ground acid-grade fluorspar and 66°Bé. sulphuric acid. Continuous equipment has been developed for this operation, but the original method of batch distillation from cast-iron retorts connected to water-cooled lead condensers is still used to a limited extent.

Lead fluosilicate may be prepared by dissolving lead carbonate or white lead in fluosilicic acid, but when required in quantity, as for the initial filling of a refining circuit, it is preferable to use electrolytic dissolving cells. These are horizontal cells with pig-lead anodes covering the bottom area and a perforated lead cathode suspended near the top. Acid is fed at a slow rate to the top of the cell, and the lead fluosilicate, which stratifies in the lower portion of the electrolyte by virtue of its high specific gravity, is removed through a siphon overflow. A current density of 30 to 50 amp. per sq. ft. of anode surface is suitable for these cells.

Acid Loss.—Under proper operating conditions, the over-all loss of fluosilicic acid from the electrolyte will not exceed 3 lb. of H_2SiF_6 per ton of refined lead produced.

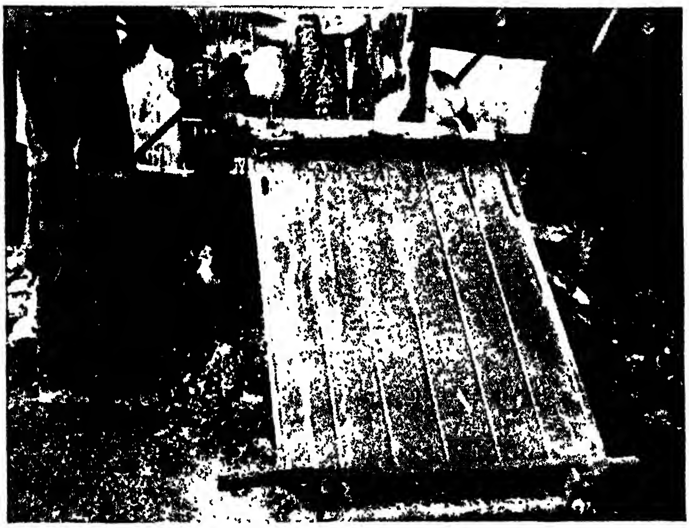

FIG. 6.—Starting-sheet pouring table, with integrally cast type of cross rod at bottom.

Much larger losses were at one time experienced, especially when relatively impure bullion was treated. These excessive losses have been eliminated by fundamental improvements in refinery construction and operating procedure.

In the first place, all mechanical losses, such as those due to inadequate cell construction, have been prevented. Limitation of the corrosion period eliminates decomposition loss at the anode and the formation of insoluble compounds such as antimony fluosilicate. Finally, and most important, is the complete recovery of solution entrained in anode slimes. Washing of the slimes must be conducted in countercurrent fashion in order to avoid the necessity for any evaporation of wash liquors. Further, the more concentrated solutions must at all times have sufficient free acid present to prevent decomposition by hydrolysis. The most effective method of washing involves the use of diffusional processes, by which the slimes are completely washed before their removal from the surface of the anode scrap[3, 6]. This is accomplished by advancing the corroded anodes through a series of dip tanks, in which they remain for a sufficient period to attain equilibrium with successively decreasing concentrations of acid and wash-water. This procedure is applicable only when the anodes contain sufficient impurities to produce a perfectly adherent slime blanket.

In normal operation, the lead content of the electrolyte increases slowly, in spite of the fact that the acid losses occurring are largely in the form of lead fluosilicate; this is due to the fact that the current efficiency is slightly lower at the cathode than at the anode, and to the small amount of lead that is dissolved chemically from the electrodes. To maintain normal composition, this excess lead is periodically removed, usually by the addition of sulphuric acid. An alternate method of lead removal is to electrolyze with graphite anodes, whereby lead peroxide is deposited at the anode while metallic lead is deposited at the cathode. Occasionally, however, a decrease in the lead content of an electrolyte may occur in operation, which is almost infallibly a danger signal indicating that an abnormal acid loss also prevails.

Construction and Operation.—Cells built of reinforced concrete have replaced the wooden tank construction originally used. They may be lined either with asphalt,

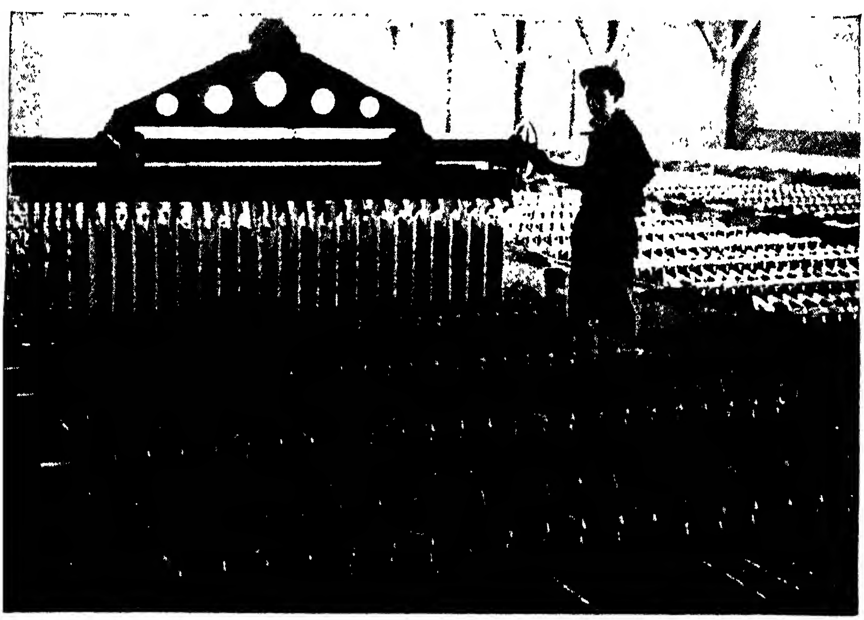

FIG. 7.—Corroded anodes being removed from cell, with short-circuiting bar in position at right end of tank.

resinous organic compounds, or by a recently developed method of impregnation with hot paraffin. Cells are arranged in cascade at the Trail plant; others use the side-by-side arrangement of the Walker system. Electrolyte is circulated at a rate of 2 to 5 gal. per min. per cell, usually entering the cell at the top and overflowing through a hard-rubber pipe extending within a few inches of the bottom. Centrifugal pumps of bronze or rubber-lined construction are used for electrolyte handling. Rubber-lined steel pipe is most satisfactory for cell feed lines, and rubber-lined launders for overflow return.

Anodes are cast in open horizontal cast-iron molds, which are generally mounted on a mechanically driven casting wheel. They are normally 24 to 26 in. wide by about 36 in. deep in body dimensions, with integral lugs or ears for suspension and handling. The thickness required, at usual current densities, is about ⅛ in. per day of anode life, plus ⅛ in. for the residual core sheet. It is important that anodes are cast to uniform weight and even thickness, in order to avoid excessive scrap and still ensure an unbroken core sheet at the end of the corrosion period. This requires a smooth-

running casting wheel with a rigid deck, molds carefully leveled, and, preferably, an automatic metering type of pouring device. The anode scrap, which is approximately 40 per cent with 4-day anodes, is of course remelted and cast in the same manner as the original bullion. At the tank house, the anodes are placed in racks in which they are properly spaced for transfer to the cells, the usual spacing being 4 to 4½ in. center to center.

Cathode starting sheets are made by pouring a small quantity of refined lead from a tilting trough on to a cast-iron plate set at a small angle to the horizontal, on which the lead freezes in a uniform sheet about 1⁄32 in. thick. These sheets are supported in the cells from cross rods of hard-drawn copper to which they are attached by looping and spot-welding. Alternatively, the cross rod may be formed of copper-plated steel, with a dovetail slot into which the sheet is integrally cast. Starting sheets may be

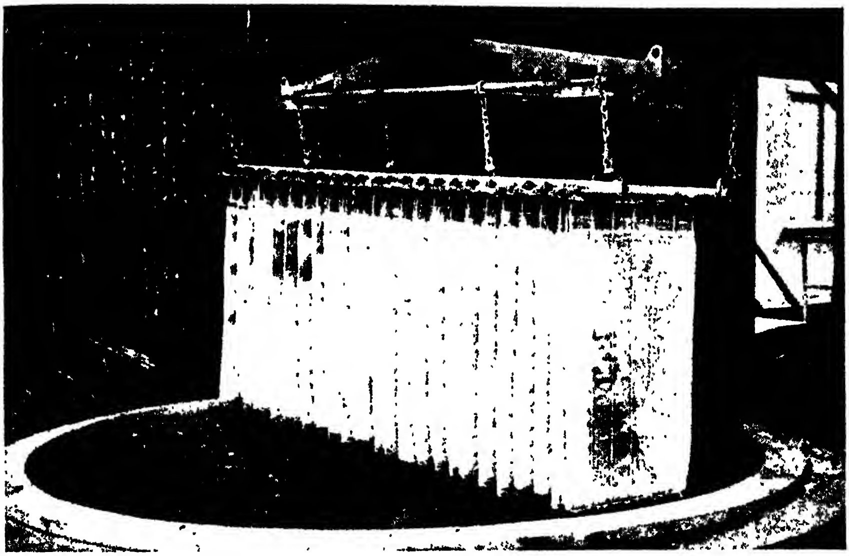

FIG. 8.—Cathodes being lowered into refined lead kettle.

stiffened considerably by grooving the casting table to form shallow corrugations, but at best are flimsy and require manual straightening before hanging in the cells. It is customary to fold over a small diagonal flap at each bottom corner of the sheet at the same time.

The deposited cathodes, weighing about 150 lb. each, are washed in a dip tank or by sprays upon removal from the cells and charged to welded steel melting kettles of 70 to 235 tons capacity. If integrally cast cross rods are used, these are skimmed from the surface of the lead after melting. Each kettle lot of refined lead is stirred or air-blown at 520°C. to remove glue ash and traces of residual impurities, sampled, and cast into standard bars of approximately 100 lb. Vertical centrifugal pumps are used to transfer the lead to the casting wheel. Casting temperatures may range from 375 to 425°C. From 1½ to 2 per cent of oxide dross is produced in the melting and casting operation, which is either returned to a smelter or reduced to common lead in a small reverberatory furnace.

Both anodes and cathodes are handled to and from the cells in complete sets, usually 24 anodes and 25 cathodes, by overhead traveling cranes provided with special hooks, the cells being short-circuited individually for the few minutes required for this operation. At infrequent intervals, cells must be shorted out of the circuit for a

sufficient time to permit draining, cleaning, and inspection of the lining. If production schedules permit, an entire cell block or group is usually cut out together for this purpose.

Corroded anodes are advanced through the wash tanks by overhead cranes, if dip washing is used, the spacing between anodes being first closed up to permit four sets of anodes to be handled together. The slimes are then removed by passing them between revolving fiber brushes or by scraping and brushing in the case of very hard slimes. If dip washing is not practiced, the slimes must be brushed off in a tank of electrolyte and carefully washed by countercurrent decantation. The washed slime may be dewatered in a filter press or centrifuge, and further dried to a moisture content sufficiently low to permit charging to the melting furnaces. In the case of dip-washed slimes, the slurry from the brushing machine is fed directly to a steam-heated atmospheric double-drum drier, which reduces moisture content to a low percentage in a single operation. Briquetting the slimes under heavy pressure at this point will increase the efficiency of the subsequent melting operation, but this practice has not yet been applied commercially.

Slime Treatment.—The details of subsequent slimes treatment are naturally variable, being determined by the composition and relative importance of the contained values. A number of wet methods of treatment have been proposed, but none has been widely used. When, as is often the case, the precious metal values are the primary concern, the general procedure is as follows: The slime is melted in a reverberatory furnace and the metal transferred to a furnace with submerged tuyères and blown with air. The major portion of the arsenic and antimony is thus removed by volatilization as oxide fume, which is collected in a baghouse connected to the flue system. Slags removed from the early stages of the operation contain the remainder of the arsenic and antimony and the majority of the lead present; as the oxidation proceeds, the residual lead is slagged off together with bismuth, copper, and tellurium. The final stages of the oxidation are conducted in a separate furnace, in which the tuyères may be above the metal bath, and to finish the charge, soda ash and niter are added to complete the removal of the tellurium and copper. A doré bullion assaying at least 99 per cent silver plus gold is tapped from this furnace and cast into shapes suitable for acid or electrolytic parting. The slags and baghouse fume are re-treated separately for recovery of their contained values, including the small proportion of the silver and gold which they carry. Slags from certain stages of the oxidation are often segregated to facilitate recovery of a particular element, such as bismuth.

Electrochemical Series.—Reference has been made in this chapter several times to the electrochemical position of the elements. In the following arrangement each element is electronegative to those that follow and electropositive to those that precede it: Cs+, Rb, Na, Li, Ba Sr, Ca, Mg, Al, Cr, Mn, Zn, Ga, Fe, Co, Ni, Tl, In, Pb, Cd, Sn, Bi, Cu, H, Hg, Ag, Sb, Te, Pd, Au, Ir, Rh, Pt, Os, Si, C, B, N, As, Se, P, S, I, Br, Cl, O, F −. The order varies slightly according to the acid radical and according to dilution, but it is a good guide for experimental work.

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CHAPTER XIV

THE ELECTROLYTIC ZINC PROCESS

By Frederick Laist,[1] Russel B. Caples,[2] and Guy T. Wever[3]

Definition.—Metallic zinc is extracted from its ores by two main methods, pyrometallurgical and hydroelectrometallurgical. The older pyrometallurgical operation, commonly referred to as the "retort process," depends on the reduction of zinc oxide to the metallic state by carbon. The hydroelectrometallurgical operation, commonly referred to as the "electrolytic-zinc process," is a much later development in which roasted zinc ores are leached in dilute sulphuric acid and the zinc obtained in the metallic state by electrolysis of the resulting solution. Zinc produced by this method is called "electrolytic zinc" to distinguish it from the "retort zinc" produced by the retort process.

The electrolytic-zinc process was originally confined to the complex lead-silver ores of zinc not well suited to the retort process. Further developments of the process have enabled it to be applied to almost any type of zinc ore.

Many variations of the electrolytic process have been investigated, both as to the zinc salt to be electrolyzed and as to the method of preparing the solution. The only successful large-scale operations have used dilute sulphuric acid leaching and electrolysis of the resulting zinc sulphate solution. This method is cyclic in that it uses the dilute sulphuric acid formed during the electrolysis of zinc sulphate solution as the source of acid for leaching additional material. The use of zinc chloride solution in the electrolytic-zinc process has never met with any outstanding success. The only commercial unit of this kind was the small plant of Brunner, Mond and Co., England, operated between 1896 and 1924, with a capacity of 5 to 10 long tons of zinc per day. Since that time no commercial plant has operated using zinc chloride solutions. Several companies have experimented with the electrolysis of fused zinc chloride; but this method has never been found satisfactory.

History.—It has been known for more than 75 years that zinc could be deposited from its solutions by electrolysis, but no attempt was made to apply this knowledge on a large scale as a method for producing zinc from its ores until about 1880. Processes employing both zinc chloride and zinc sulphate solutions were tried from time to time without marked commercial success. In 1914, the Anaconda Copper Mining Co. at Anaconda, Mont., and the Consolidated Mining and Smelting Co. at Trail, B. C., began independent investigations of the process as a means of solving the problem of treating complex ores occurring in their respective districts. Both were sufficiently successful to justify the erection of small test plants which were rapidly enlarged as the war demand for high-grade zinc developed. Later, the Australian zinc producers were attracted by the successes of these companies and, after a thorough investigation of the process and of the results obtained, built a plant at Risdon, near Hobart, Tasmania, for the treatment of concentrate from the Broken Hill mines.

The original plant of the Anaconda Copper Mining Co. at Anaconda, Mont., was more of a pilot plant for the development of the process than a commercial unit,

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but before dismantlement it was producing more than 25 tons of zinc per day. A plant having a capacity of 100 tons per day was constructed at Great Falls, Mont., in 1916. The Great Falls plant was located near the source of power, because it was more economical to transport the materials to be treated than to transmit the power. Shortly after the Great Falls plant started operations, the pilot plant at Anaconda was abandoned. The capacity of the Great Falls plant has been steadily increased until at the present time it is capable of producing more than 300 tons of slab zinc per day. The demand for zinc was such that a plant with a capacity of 150 tons per day was built at Anaconda early in 1928. This plant has also been enlarged in recent years.

The original 60-ton plant of the Consolidated Mining and Smelting Co. at Trail, B. C., has been enlarged until it is now one of the largest producers of zinc in the world.

The Amalgamated Zinc Co. first operated a small test plant at Bully Hill, Calif., the material treated being concentrate shipped from Australia. This work was the basis for the construction of a 10-ton unit at Risdon, by the Electrolytic Zinc Co. of Australia. After a year or so of operating this plant, it was decided to abandon it and construct a 100-ton plant. The Risdon plant is now ranked among the larger zinc producers.

These companies were the pioneers in the successful commercial application of the electrolytic-zinc process, and all use the same basic process. These plants have found that, for the electrolysis of zinc sulphate solution, a normal current density of 30 to 40 amp. per sq. ft. of cathode surface is the most satisfactory for their particular needs. This is considered a low current-density operation.

After these plants had demonstrated the commercial success of the process over a period of 10 years, many new plants were built in widely scattered parts of the world. Most of these plants employ processes closely resembling those developed in the pioneer plants.

The Sullivan Mining Co. operates a plant of considerable capacity near Kellogg, Idaho.[1] The outstanding feature of this plant is that it uses the Tainton high-density high-acid process. Shortly after this plant was completed, the Evans-Wallower plant, at East St. Louis, Ill., was built. This plant, also using the Tainton process, was operated for only a short time. In 1940 it was rebuilt by the American Zinc Co. for a low-acid low-density process as in general use elsewhere.

The early attempts to use sulphuric acid leaching were failures mainly because the experimenters failed to realize that a very high purity of solution was necessary for the successful electrolysis of zinc-sulphate solution. Once this fact was recognized, and suitable methods of purification were developed, the ultimate success of the electrolytic-zinc process was assured. Many important details remained to be worked out, but the fact that, with a sufficiently pure solution, zinc could be successfully deposited from an acid solution gave the process enough promise to justify the expense of developing the necessary methods.

Most electrolytic-zinc plants follow the same basic methods, but are highly individualistic in their applications of the process. The problems encountered by

[1] This plant is often referred to as the Silver King plant, because of its situation. The original plant was described by U. C. Tainton and E. T. Leyson in Vol. 70, *Trans. A.I.M.E.*, p. 486, 1924. In Vol. 121, p. 527, 1936, W. G. Woolf and E. R. Crutcher bring the information concerning this plant up to that date. There have been various high-density plants built here and abroad since the original Sullivan installation, one of the most recent being that at Corpus Christi, Tex., which has been well covered by G. H. Cunningham and Allen C. Jephson in Vol. 159, *Trans. A.I.M.E.*, p. 199, 1944. If detailed information on the high-density zinc process is desired, the reader is referred to these articles and to the *Eng. Mining Jour.*, Vol. 145, No. 9, pp. 64–72, 1938.—EDITOR.

each plant are so different from those of any other plant that there remains no "standard" practice that might be used as a basis for comparison.

Application of the Process.—The original idea in developing the electrolytic-zinc process was to provide a method for the treatment of complex zinc ores. Those ores were mainly lead-zinc-silver ores, most of which also contained some copper and iron and produced a concentrate rather low in zinc content—30 to 40 per cent. These concentrates were not well suited to the retort process. There is now no doubt of the superiority of the electrolytic process for the treatment of ores of this class where power is available at a comparatively low rate. Higher recoveries of all metals present and lower operating costs per pound of zinc are the two main advantages of this process.

The concentrates originally treated at Anaconda and Great Falls contained less than 35 per cent zinc and about 15 per cent iron. Improvements in concentration practice since that time have made possible the separation of zinc and lead in many ores of this class, with the production of a much higher grade zinc concentrate. This higher grade concentrate contains much less lead, iron, and silver than formerly encountered and has proved particularly adaptable to the electrolytic process.

One essential requirement of the electrolytic process is a large source of power, the cheaper the better. Most of the large electrolytic-zinc plants have been located close to the source of comparatively cheap water power. Power is the largest single item of cost in the operation, and it is necessary to obtain the lowest rate possible. The lower the rate of power, the wider the range of ores that can be economically treated. It is not vitally necessary that water power be available, as cheap power can be generated from coal in some localities and then transmitted to the source of ore supply. The saving of freight on both ore and coal can then be applied as a credit to the cost of producing power. The amount of coal and coke required by a retort plant using coal for fuel is just about sufficient to produce the power required for an electrolytic plant of the same capacity. Within reasonable distances, it is cheaper to generate power at the source of fuel and transport it to the ore supply, than it is to ship the coal. Water power is in most cases cheaper than power generated from coal, but usually it must be developed in large units to be economical. It may be that some possible sources of water power, not now utilized because of the lack of sufficient demand near by, may eventually be developed for the location of electrolytic-zinc plants. The total requirement for a plant producing 100 tons of electrolytic zinc per day is about 20,000 hp.

From the standpoint of labor requirements and working conditions, the electrolytic process compares favorably with the best of the industrial plants. For the production of 100 tons of zinc per day from a concentrate containing 55 per cent zinc, less than 200 men are required. A large number of these are comparatively unskilled labor. A high class of labor is attracted, making for a steady and dependable supply of labor of more than average efficiency.

The cost of construction of an electrolytic-zinc plant is necessarily high, owing to the large amount of copper, lead, and aluminum required for bus-bar lines, electrodes, electrode support bars, solution piping, acidproof pumps, and other acidproof equipment. The high salvage value of an electrolytic-zinc plant offsets the heavy first cost. The cost of buildings for an electrolytic-zinc plant need be no more than for a retort plant of like capacity. The difference in cost between the two is mainly for the equipment contained in the buildings. When the high salvage value of an electrolytic plant is credited to the cost of construction, the ultimate difference in cost between it and a retort plant will be little, if any, in favor of the retort plant.

The normal production of a high-purity zinc is a large factor in favor of an electrolytic-zinc plant. Zinc of high purity usually commands some premium over the

lower grades. *It is possible for an electrolytic plant to furnish zinc of any specified analysis, varying either the cadmium or lead content to suit the customer.* Any grade up to the "electrolytic" grade with a purity of 99.99+ per cent can be produced. In fact it is quite common for an electrolytic plant to produce all its cathode zinc with a high degree of purity and to debase a portion with cadmium or lead during melting and casting, in order to meet customers' specifications.

The high recovery of metals other than zinc by the electrolytic process, and the comparatively small amount of residue produced, will, in some cases, result in the production of a residue of sufficient value to pay the cost of treatment. A high recovery of lead from electrolytic-plant residue may be obtained at moderate cost, and with some ores, the credit from residue may amount to a large item in favor of the electrolytic process.

Combinations of circumstances are possible that will eliminate either the electrolytic or the retort process from consideration for the treatment of any class of ores in any locality; so both processes should be thoroughly investigated.

The large amount of soluble silica in carbonate and silicate ores is decidedly detrimental to the electrolytic-zinc process, making the separation of residue and solution a difficult problem. This problem has been successfully met by the plant of the Rhodesia Broken Hill Development Co., Broken Hill, Northern Rhodesia. This plant produces zinc by the electrolytic process from ore containing 25 per cent zinc in the form of silicate. The outstanding feature of the process used is the conditioning of the leach pulp, by careful control of temperature and acidity, to convert the gelled silicic acid into the granular form.

There are isolated instances in which certain impurities, such as arsenic, antimony, cobalt, nickel, and germanium, occur in such amounts as to add greatly to the cost of solution purification in the electrolytic-zinc process. These classes of ores can be more economically treated by the retort process.

The electrolytic process is particularly suited to the treatment of concentrates produced by the flotation method. The smaller the particle size of the concentrate to be roasted, the lower the temperature necessary to eliminate the sulphur content. Also, finely ground calcine is essential for the satisfactory leaching of roasted concentrate. A large proportion of zinc concentrate now produced is flotation concentrate, especially since the general application of selective flotation to ores containing both zinc and lead.

Outline of the Process.—An arbitrary division of the electrolytic-zinc process groups the necessary operations under three divisions: (1) the preparation of ore or concentrate for leaching, (2) the treatment of roasted ore or concentrate to produce a pure solution of the zinc salt to be electrolyzed, and (3) the electrolysis of the pure solution to produce metallic zinc and to regenerate the leaching solution.

Preparation of Concentrate for Leaching.—Concentrates containing zinc sulphide must be roasted to convert the zinc sulphide present into zinc oxide or zinc sulphate. Zinc sulphide is insoluble in the leaching solution, while zinc oxide or zinc sulphate is readily soluble. The conditions under which roasting is carried on also control to some extent the solubility of iron, copper, and silver in the leaching solution. Roasting is one of the most important steps in the electrolytic process, especially when leaching with dilute sulphuric acid, as the possible recovery is greatly dependent upon how well this step is performed. Several methods of preparing the concentrate, other than roasting, have been proposed. None of these is commercially feasible at the present time.

Production of Pure Zinc Solution.—Dilute sulphuric acid is the only solvent used in the leaching of roasted ore or concentrate for the commercial production of electrolytic zinc. Not only zinc but many other elements, if present in the roasted

material, are dissolved by dilute sulphuric acid. Most of these elements must be removed from solution to ensure successful electrolysis. The production of a pure solution is really a combination of several steps: leaching to dissolve zinc, separation of solution and insoluble residue, purification of solution, and clarification of solution. This combination is of basic importance to the process as, given perfect roasting, the recovery of zinc is dependent on proper leaching and filtration, and the successful electrolysis of zinc sulphate solution is dependent on proper purification of solution.

Electrolysis of Solution.—The only successful commercial method so far developed for the production of metallic zinc from zinc sulphate solution is by electrolysis. Purity of solution is the essential factor. Probably no other process operating on such a large scale requires the same degree of purity. Other factors influencing electrolysis are the temperature of the electrolyte, current density, ratio of acid to zinc in the electrolyte, period of deposition, and purity of electrodes. Lead or lead-alloy anodes and aluminum cathodes are used. The current applied varies from 30 to 100 amp. per sq. ft. of cathode surface. Purified zinc sulphate solution is fed to the electrolyzing cells where, by the application of an electrical current, zinc is deposited as a metal on the cathode. For each unit of zinc deposited, approximately one and one-half units of acid are regenerated. The efficiency of this reaction decreases rapidly as the ratio of acid to zinc increases. For this reason no attempt is usually made to remove more than about 75 per cent of the zinc in solution. The spent electrolyte, containing about 25 per cent of the original zinc and the acid regenerated during electrolysis, is returned to the leaching division to be used for further leaching of roasted concentrates. The zinc deposited during electrolysis is removed at the end of regular periods and is melted and cast into slabs.

Zinc is electronegative to hydrogen, and it would be expected that zinc could not be deposited from an acidified solution of zinc sulphate. The hydrogen overvoltage on zinc, however, is high enough so that zinc plates out in preference to hydrogen. Some hydrogen is always evolved, especially with the higher current densities.

The simple chemical reactions involved in the roasting, leaching, and electrolysis of zinc are as follows:

Roasting:

$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$
$$2ZnO + 2SO_2 + O_2 = 2ZnSO_4$$

Leaching:

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O$$

Electrolysis:

$$ZnSO_4 + H_2O + \text{direct current} = Zn + H_2SO_4 + \tfrac{1}{2}O_2$$

In addition to the divisions of the process as outlined, there might be added a fourth, treatment of the residue. The electrolytic-zinc process is particularly applicable to the treatment of the complex ores of the Western states, and there are in nearly every instance sufficient values in the residue to warrant their recovery.

The great variety of ores to which the process is applicable results in the production of several classes of residue. Each class of residue requires its own method of treatment to produce the greatest possible return. Lead smelting, copper smelting, wet methods, or a combination of methods, may be necessary depending on the class of residue produced.

PREPARATION OF CONCENTRATES FOR LEACHING

Roasting.—The main object of roasting for the electrolytic-zinc process is to obtain the maximum percentage of zinc that will be readily soluble in the leaching

solution. Zinc sulphide is practically insoluble in dilute sulphuric acid at ordinary temperatures. Zinc oxide is readily soluble in dilute sulphuric acid, and zinc sulphate is soluble in water. Roasting is done, therefore, to convert the zinc sulphide in the unroasted concentrate as completely as possible into zinc oxide and zinc sulphate. Only enough zinc sulphate to supply the acid requirements of the plant is normally desirable, as any excess must eventually be discarded. The acid requirements of a plant of this kind are usually small. The only acid losses are as insoluble sulphates and solution losses. The higher the lime and lead content of the concentrate, the greater will be the loss as insoluble sulphates. The chief loss of solution is as entrained moisture in the residue. Usually a zinc sulphate formation of 2 to 3 per cent sulphate sulphur in the calcine is sufficient to supply all acid losses. A greater amount of zinc sulphate than necessary tends to build up zinc and acid in the system. A higher concentration of zinc in the solution results in a greater loss of zinc in the residue and increases the difficulties of settlement and filtration.

Roasting Furnace.—Most electrolytic-zinc plants use some modification of the Wedge furnace for the roasting of zinc concentrates. The Wedge furnace is a circular multiple-hearth furnace of the McDougall type. Nearly every electrolytic-zinc plant using this furnace has developed some modification in design, until at the present time, as far as the electrolytic-zinc industry is concerned, there exists no standard form. Figure 1 shows the form of Wedge furnace from which these modifications were derived.

The type of Wedge furnace used by the Anaconda Copper Mining Co. at its Great Falls and Anaconda plants is 25 ft. in diameter. It has seven superimposed roasting hearths plus a top hearth for drying the feed. A 5-ft.-diameter hollow steel brick-lined revolving center shaft carries 26 cast-iron arms, four for each of the drier and first hearths, and three for each of the remaining six hearths. All the arms except those on the drier hearth are cooled with water delivered to the arms through a system of piping inside the center shaft. The center shaft is supported on a step bearing and, complete with bricks, arms, piping etc., weighs approximately 50 tons. The speed of the center shaft varies in individual furnaces from one revolution in 4 min. to one revolution in 2 min. The driving mechanism consists of a set of reducing gears powered by a 15-hp. 555-r.p.m. electric motor. The furnaces are fired with natural gas, usually by two burners on the seventh or bottom hearth, spaced 180 deg. apart. When additional heat is desired in other parts of the furnace, portable burners are set up in the furnace doors.

The concentrate to be roasted is fed by an apron feeder driven from the revolving center shaft. It is discharged from the feeder onto the outer edge of the drier hearth and advanced across the hearth by means of rabbles or rakes fastened to the furnace arms. When the material reaches the inside of the drier hearth, it falls through holes to the next hearth below, the first roasting hearth. The rakes on the rabble arms of the hearth are set to move the material outward; when it reaches the outer edge of this hearth, it falls through drop holes onto the next hearth, and so on down through the furnace. The roasted material, commonly called calcine, is discharged from the seventh, or lowest, hearth into two steel hoppers provided as a temporary storage for calcine. These hoppers discharge into cars for removing the calcine.

The gases produced by the roasting process pass upward through the furnace countercurrent to the material being treated. From the first roasting hearth, the gases are passed into offtake flues that lead to the main gas flue. The roasting of flotation or fine table concentrates in this type of furnace is productive of a large amount of flue dust which must be collected and returned to the furnaces for further treatment. A part of the dust settles out in the flues adjacent to the furnaces. These flues are hoppered to facilitate removal of this dust, which is ordinarily returned to

the furnace where it was produced. A large portion of the dust, however, is collected very efficiently by a Cottrell precipitator and is fed to a furnace operating on flue

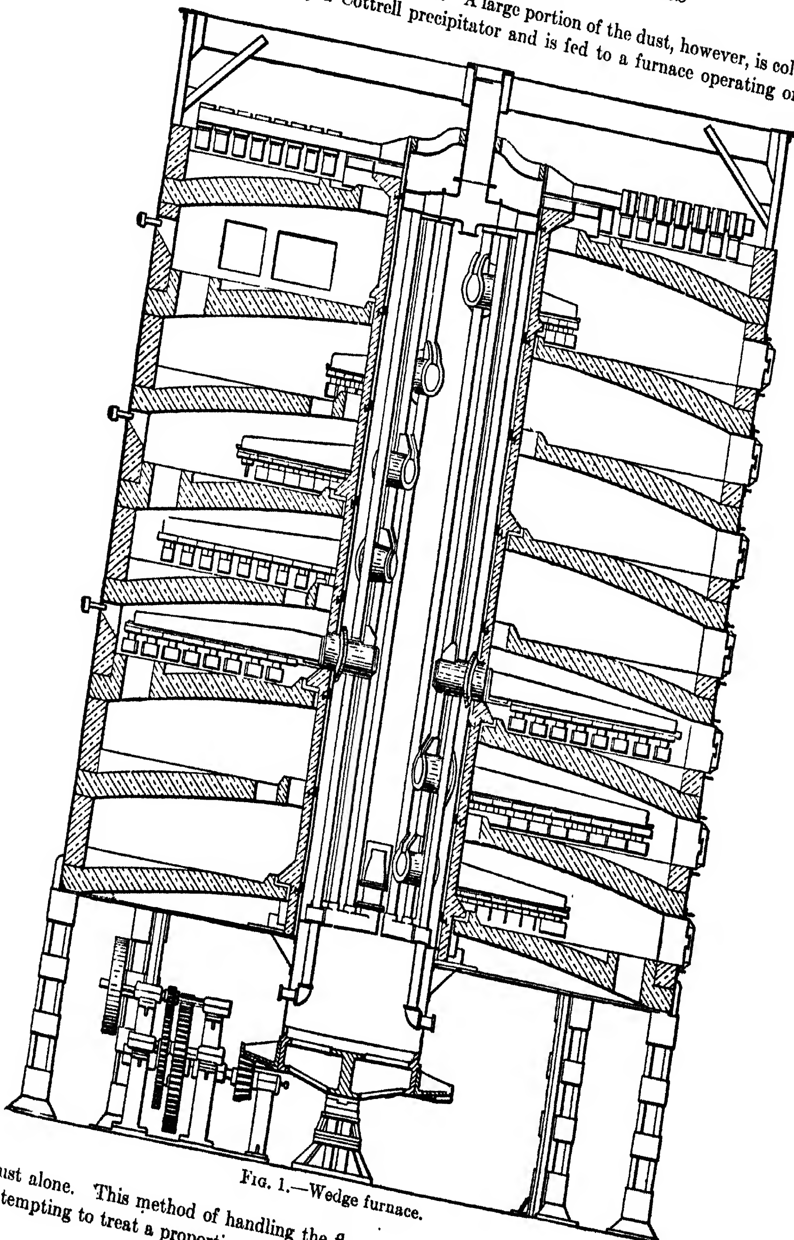

Fig. 1.—Wedge furnace.

dust alone. This method of handling the flue dust is much more satisfactory than attempting to treat a proportional amount of dust through each individual furnace.

The materials to be treated are flotation or fine table concentrates, over 50 per cent of which will pass a 200-mesh screen. The calcine product from the roasting furnaces contains a certain amount of oversize material that is screened out, crushed, ground, and returned to the furnaces for further treatment. Dust collected from the furnace flues is also re-treated through the furnaces. These last two materials contain an appreciable amount of unroasted matter which must be further oxidized before they are suitable for leaching purposes.

The amount of flue dust carried away from a furnace during roasting depends in large part on the fineness of the concentrate and on the volume and velocity of the flue gases. The amount of dust that can be carried by a gas of given volume depends mainly on the velocity of the gas stream. A reduction in velocity of a given volume results in an even greater reduction in the maximum load of dust that can be carried by that given volume of gas. In order to keep down the amount of flue dust produced by the furnace, it is necessary to keep the gas volume and velocity as low as possible by carefully regulating the door openings on each hearth to give only the amount of air necessary for roasting and for cooling the upper hearths. Ordinarily the Wedge furnace has but two gas offtake flues. The addition of one or more offtakes lowers the velocity of the gases very materially and allows more air to be admitted to the furnace without increasing the amount of flue dust produced. If a large portion of the dust collected from the flues is returned to one furnace (or more if necessary) and the gas volume on this furnace is held as low as possible, the amount of dust recirculated may be kept at a minimum.

The capacity of this type of furnace varies widely with the class of material treated. The amount of lead contained in the concentrate has a large effect on the amount that can be treated. The capacity of a furnace is greater for high-zinc concentrate containing relatively low lead values than for a lower grade high-lead concentrate. The limiting factor for low-zinc complex concentrates is the ability to cool the upper hearths without undue production of flue dust. In general, the higher the zinc content of the concentrate, the higher the roasting temperature required. The normal limits when roasting a high-grade zinc concentrate are 40 to 60 tons of new feed per 24 hr.

Lump coal, pulverized coal, oil, and gas have all been used as fuel in these furnaces. Gas is by far the most satisfactory. A large part of the ash from pulverized coal settles in the furnace and flue system and eventually finds its way out in the calcine. Then it adds to all subsequent operating costs, such as leaching, filtration, and residue treatment. Fuel requirements vary with the class of concentrate being roasted. When using pulverized coal containing a heat value of 10,000 B.t.u., the observed limits are from 7 to 18 per cent of the weight of concentrate. Oil requirements are about 20 per cent less than coal on a heat-unit basis of comparison. Gas requirements vary from 2500 to 3500 cu. ft. of 1000 B.t.u. gas per ton of concentrate.

The electrolytic-zinc plant of the Consolidated Mining and Smelting Co. of Canada, at Trail, B. C., has developed a "burning concentrate process" of roasting zinc concentrates. This method, also known as "flash roasting," under some conditions has decided advantages over the conventional method. The original roasting practice at Trail employed standard Wedge furnaces. Eight of these furnaces were converted to flash roasting by removing the second, third, fourth, and fifth hearths from each furnace to form a combustion chamber.

The top or drier hearth is covered and, along with the regular first hearth, is used to dry completely the wet concentrate feed. Some gas from the combustion chamber is by-passed through this chamber to aid in the drying process. The wet concentrate is fed at a controlled rate to the drier hearth through a closed chute. After being thoroughly dried while passing over the two drier hearths, the material is then delivered

to a ball mill situated near the furnace. The ball mill pulverizes all lumps formed during the drying process. The discharge from the ball mill is then elevated to storage hoppers over each furnace.

The material at this point is fine, dry, and at about 95°C. It is fed from the storage hoppers by air injectors which deliver it to the burner. At the burner it is mixed with air supplied by a fan and is blown into the top of the combustion chamber of the furnace. The material ignites immediately upon entering the furnace, and in burning maintains a temperature between 900 and 950°C. in the combustion chamber. No external heat is needed to maintain the roasting temperature, as all heat is supplied by the burning concentrate itself. The temperature of the combustion chamber is maintained between very close limits by carefully controlling the ratio of concentrate to air.

About 40 per cent of the material introduced into the combustion chamber is carried out of the furnace with the flue gases. The hot dust and flue gases pass through waste-heat boilers where approximately 1.1 lb. of steam is generated for each pound of concentrate treated. The gases pass from the boilers into cyclone collectors where most of the dust is removed. The remaining dust is then removed by passing the gas stream through a Cottrell precipitator.

The material settling to the bottom of the combustion chamber of the furnace, comprising about 60 per cent of the total, is rabbled across two collecting hearths at the bottom of the furnace. There the remaining sulphide is oxidized, and the finished calcine is then carried to a calcine storage by means of conveyors. The collecting chamber can, if necessary, be used as a sulphating chamber by the introduction of a strong atmosphere of sulphur dioxide. Under normal operating conditions, the calcine from the flash-roasting furnaces at Trail assays, on the average, about 0.3 per cent sulphide sulphur and 0.4 per cent sulphate sulphur.

The capacities of the suspension-type roasters at Trail have been increased by the introduction of oxygen into the furnace during roasting. The oxygen is obtained as a by-product from an ammonia plant.

The zinc roasters of the Gieschе Spolka Akcyzna, Poland, have been changed over to suspension roasting. No heat recovery has been attempted, and the roaster gases are taken off the top of the furnace. It was found necessary to grind the flotation concentrates to obtain thorough roasting.

The advantages of this method of roasting are: more than doubling the furnace capacity, saving in cost of fuel, and production of gas rich enough in sulphur dioxide or acid manufacture. The disadvantages are: production of a much greater percentage of flue dust, higher gas temperatures, and the drying and grinding of concentrate.

The advantages outweigh the disadvantages heavily where fuel is expensive and acid is to be produced from the flue gases. Also, where large quantities of steam can be utilized, the waste-heat boilers are a decided advantage. By proper control of the air supplied to the furnace, fusion of the roasted particles is avoided and the resulting calcine can be leached without difficulty.

The Flin Flon plant of the Hudson Bay Mining and Smelting Co. uses modified Wedge-type roasters operating on the "split-draft" process. This type of furnace is equipped with gas offtake flues on both the first and seventh hearths. Under normal operating conditions, the draft splits at the third or fourth hearth, with about one-fourth the gas leaving the furnace from the first hearth. By regulating the amount of gas drawn from the upper or lower offtakes, the location of the heat zone in the furnace can be controlled. The amount of concentrate fed to the furnace is so regulated that the heat of combustion of the concentrate is enough to maintain roasting temperature. While no external heat is used for normal operation, several stand-by

burners using pulverized coal are installed on each furnace to be used in case of necessity and for heating the furnaces when starting up after a shutdown period.

The electrolytic plants at Ordzhonikidze and Cheliabinsk, U.S.S.R., each have six 25-ft.-diameter roasters designed to operate on the split-draft principle. The split-draft process permits the heat of combustion to be used under full control and elimi-

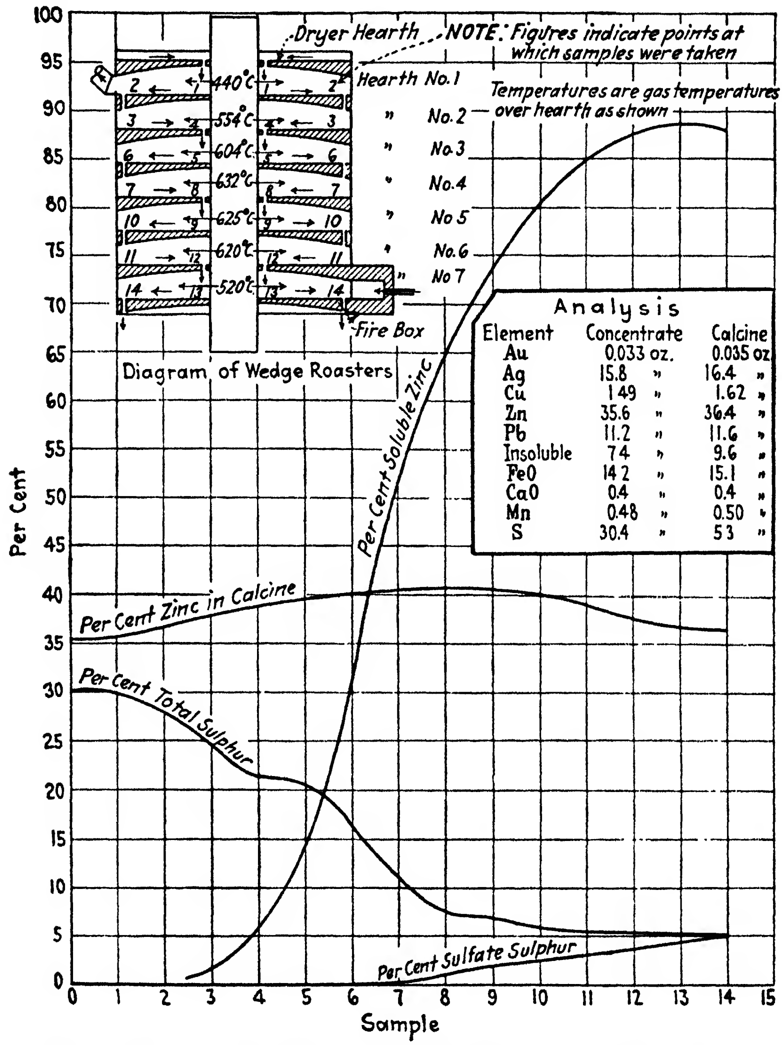

FIG. 2.—Roasting low-grade concentrates without returning flue dust.

nates the use of extraneous fuel. It permits a close control of sulphation, gives consistent low operating temperatures with a low ferrite formation, and increases the life of the roaster bricks and rabble arms.

The Electrolytic Zinc Co. of Australasia, at Risdon, Tasmania, has a somewhat different roasting practice from most other zinc plants. The material delivered to the Risdon plant is not raw concentrate but has been preroasted before shipment. This material when delivered contains about 7 per cent sulphur with about 6 per cent

as sulphides. It is wetted before shipment with water relatively high in chlorine and, being carried by ships, is also liable to accidental wetting with sea water.

The furnaces are of Risdon design and are a modification of the Leggo furnace used for roasting arsenical pyrites. Each furnace has four superimposed hearths 85 × 8 ft. Each hearth has a flue connecting to the main flue system. The furnace charge is fed on to the top hearth through a hole in the top, and from this hearth to the lower hearths through regulated openings. Each hearth is practically a separate furnace. The furnace is built on a slope of 1 : 12 and has 16 columns which carry the rabble arms for each hearth. The sweep of each rabble arm overlaps the sweep of the next in line, and by this means the material is carried the length of the furnace. Each furnace treats about 90 tons of charge per day, with a fuel consumption of 10 to 12 per cent of the weight of the charge. The fuel used in the furnaces is slack coal burned on a traveling-grate stoker.

The Formation of Ferrites.—The presence of iron in zinc sulphide ores causes the greatest loss in the electrolytic-zinc process. Under certain conditions, zinc oxide and iron oxide combine to form zinc ferrite, $ZnO.Fe_2O_3$, which is insoluble in warm dilute sulphuric acid. No successful commercial method has yet been developed to prevent the formation of some zinc ferrite during roasting, but its formation can be partially controlled by a careful regulation of roasting conditions. The formation of ferrites is dependent on the iron content of the concentrate, the association of the zinc and iron content, the temperature of roasting, and the length of the roasting period. Analysis of the concentrate will not alone serve as a means of predicting the amount of ferrite that will be formed. A concentrate with a relatively low iron content, with the zinc and iron closely associated, will tend to form more ferrites during roasting than a concentrate with a higher iron content, but with the iron and zinc in less intimate contact.

Iron sulphide oxidizes at lower temperatures than zinc sulphide, and it is possible by careful control to make a preferential roast if the initial roasting temperature is kept below 600°C. The object is to prevent the simultaneous oxidation of iron and zinc as much as possible. Some zinc sulphide will always be roasted, however, even at low temperatures, with the subsequent formation of ferrites. If, however, the main bulk of the iron sulphide is roasted first, and the zinc sulphide later, the chances of combination are greatly reduced. When the particles of zinc and iron are very intimately mixed, as in marmatite, preferential or selective roasting is practically impossible and a high percentage of ferrite is bound to result. The general practice is to keep the temperature as low as possible throughout the furnace and, especially, to keep the temperature on the first two or three roasting hearths below 600°C. As the iron content of a concentrate increases, the possibility of making a selective roast also increases. Most low-iron concentrates roast with complete combination of the iron and zinc as ferrite. Figure 2 gives data taken from roasting low-zinc high-iron concentrate. The data in Table 1 were obtained in the laboratory on samples from the same class of concentrate and show that the analysis cannot be depended upon to determine the amount of ferrite formation.

Roasting Temperature.—Roasting depends almost entirely on the control of temperature and time. The length of the roasting period is set by the roaster speed and the design and position of the rakes on the rabble arms. While it is possible to change the speed of a furnace by a change of gearing, the speed is usually constant over long periods of time. A variation in rabbling time by a change in design and spacing of rakes is also possible but, like the turning speed of the furnace, has no flexibility of control. Therefore, the control of roasting is dependent on temperature, which is, in turn, controlled by the amount of fuel burned and the quantity of air admitted to the furnace.

TABLE 1

	Per cent Zn	Per cent Pb	Per cent Fe	Per cent S	Per cent SO_4	Per cent soluble Zn	Per cent As	Per cent Sb
Concentrate A	39.6	13.8	6.6	29.2	...	....	0.10	0.04
Calcine A	37.8	....	6.3	8.8	8.5	92.6	0.08	0.03
Concentrate B	47.3	3.4	7.0	32.2	...	....	0.53	0.17
Calcine B	44.8	....	6.6	8.5	8.1	94.2	0.23	0.05
Concentrate C	34.9	13.6	11.6	32.0	...	....	0.11	0.03
Calcine C	36.8	....	11.8	5.4	5.2	92.7	0.09	0.03
Concentrate D	34.3	17.8	7.5	28.4	...	...	0.08	0.03
Calcine D	33.8	....	7.4	6.0	5.9	89.1	0.07	0.03
Concentrate E	30.8	3.6	16.4	35.3	...	....	0.90	0.19
Calcine E	30.4	....	16.0	8.5	8.5	87.2	0.24	0.11

NOTE.—Roasts made at low temperature—650°C. maximum—with no attempt to control sulphate sulphur.

The maximum temperatures in roasting for the electrolytic-zinc process may be given as approximately 650°C. for complex low-zinc concentrates, and 750°C. for high-zinc concentrates. In order to obtain speed in roasting, the temperature must be carried as high as possible without materially lowering the solubility of the product.

TABLE 2

	Per cent Zn	Per cent Pb	Per cent Fe	Per cent S	Per cent SO_4-S	Per cent soluble Zn
Concentrate A	32.3	8.2	15.6	32.4		
Calcine A	35.0			3.8	3.2	80.3
Concentrate B	32.3	16.4	3.7	28.4		
Calcine B	34.6			3.9	3.5	88.5

The initial temperature should be well under 600°C. for at least one roasting hearth. This is especially true for concentrates containing appreciable amounts of lead and iron sulphides. Lead sulphide fuses without roasting if the initial temperature is too high and forms a hard crust on the hearth under the rakes. It may also coat the particles of zinc sulphide and form lumps that will pass through the furnace without being roasted; these must be screened out of the calcine, crushed, ground, and returned to the furnace for additional roasting. As the initial temperature increases, the loss of lead through the formation of fume also increases rapidly. High initial tem-

peratures in the presence of iron sulphides are very conducive to the formation of zinc ferrites.

With the initial temperature low, the temperature lower down in the furnace must be increased to complete the roasting of zinc sulphide and to prevent the formation of an excessive amount of zinc sulphate. This temperature must also be kept

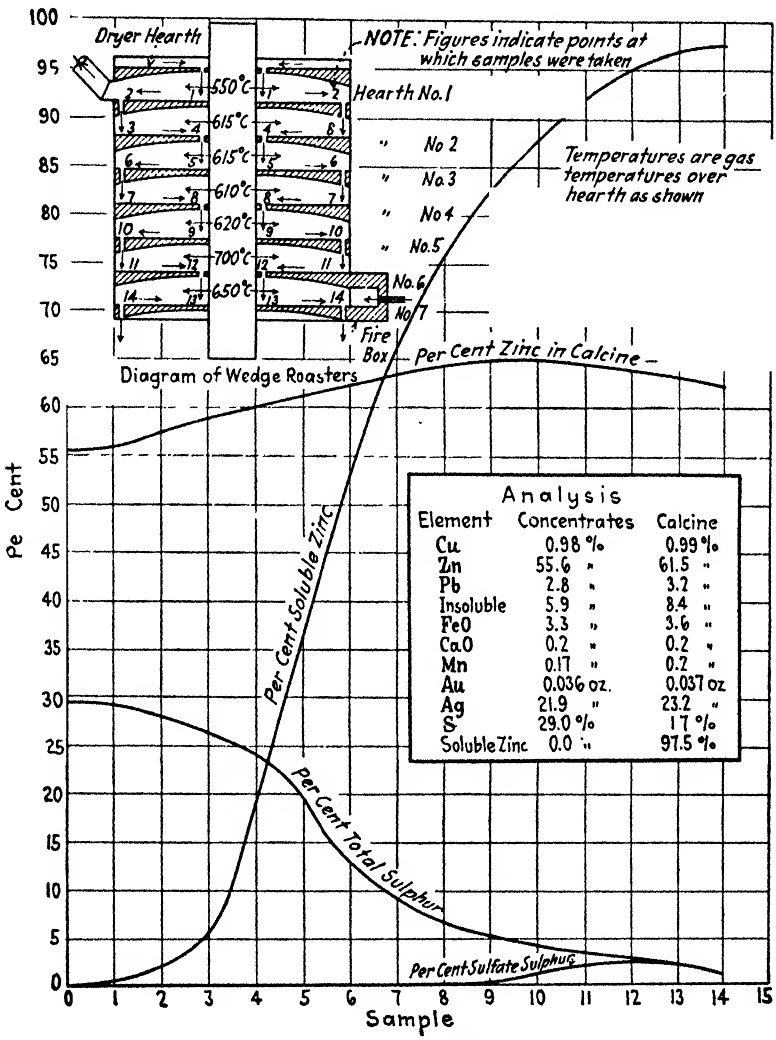

FIG. 3.—Roasting high-grade concentrates in Wedge furnace.

high enough to prevent any appreciable amount of sulphide sulphur being left in the calcine, as each unit of sulphide sulphur will hold approximately twice its weight of zinc as an insoluble compound. The temperature must not be raised too high, as an increase in temperature tends to increase the formation of zinc ferrites. Roasting then becomes a nice balance between the formation of ferrites and the amount of sulphide sulphur left in the ore.

Each concentrate treated is a problem in itself, and the best roasting conditions must be determined by actual practice. The best conditions for roasting a concentrate cannot be satisfactorily determined on a small scale, but must be tried under the actual roasting conditions in the furnace. Figures 2 and 3 give temperatures from the operation of two furnaces on widely different classes of concentrate.

TABLE 3

Hearth	Per cent SO_2	Gas temperature, degrees Centigrade	Calcine temperature, degrees Centigrade	Per cent CO_2
1	3.0	438	459	2.5
2	2.8	560	551	2.5
3	2.2	626	665	2.7
4	1.2	650	665	2.8
5	0.5	622	638	3.4
6	0.3	622	652	3.6
7	0.1	543	602	3.0

Temperature regulation in the furnace is obtained by varying the amount of air admitted into the furnace at different points, and also by varying the amount of fuel burned. The Wedge roaster radiates only a small amount of the total heat involved in the process. Some heat is conducted away by the cooling water in the arms, but is only a small part of the total. Approximately 80 per cent of the heat evolved during the combustion of zinc sulphide escapes with the flue gases. With the same zinc content, but with varying amounts of lead sulphide and iron sulphide, very different heat problems will be presented. Analysis of two concentrates and the resulting calcines taken from monthly averages in actual practice are given in Table 2. The difference of 4 per cent in sulphur content of these concentrates is due to the difference in iron content, and must be eliminated on the upper hearths, requiring more cooling air for concentrate A. If the lower part of the furnace is required to do too much roasting, the larger volume of hot gases from the lower hearths tends to raise the temperature on the upper hearths and will require more cooling air on these hearths. Too much air admitted to the hearths where sulphur is burning tends to raise the temperature still further. It is essential to keep the volume of gas as low as possible on the lower hearths if proper control of upper-hearth temperature is to be obtained without too great a total gas volume. Table 3 gives the temperatures and SO_2 analysis, by volume, of the gas on the different hearths of a furnace roasting low-zinc concentrate with excellent results. Pulverized coal was used for fuel.

Sulphate Roasting.—The term "sulphate roasting" as commonly used in connection with roasting for the production of electrolytic zinc is really a misnomer. It is not desirable to form more zinc sulphate than is required to offset the loss of acid in the leaching plant. This term was coined to apply to the set of roasting conditions necessary to supply acid for a plant using limestone or milk of lime for neutralization in the leaching division, thereby greatly increasing the loss as insoluble sulphates in the residue. In this process, unless sufficient acid was formed to offset this loss, it was necessary to add fresh acid to the system. The maximum amount of sulphate sulphur formed in practice was about 6 per cent of the weight of calcine. Ordinary

roasting practice on the same class of material would give about 3 per cent sulphate sulphur.

The chemical reactions involved in the formation of sulphate sulphur are debatable, as are all the reactions during the roasting process. In any case they are many and involved.

The reaction $ZnS + 2O_2 = ZnSO_4$ is possible, but if occurring where the temperature is high, it would immediately be broken down into zinc oxide with the formation of SO_3. Whether zinc sulphate is formed according to the reaction $ZnO + SO_3 = ZnSO_4$ or by $ZnO + SO_2 + O = ZnSO_4$ is not especially important. In either case the presence of iron as a catalyst is necessary to the reaction. Some ferrite, $ZnO.Fe_2O_3$, may also be decomposed, forming $ZnSO_4$, in the presence of a strong atmosphere of SO_2.

A furnace roasting for a certain amount of zinc sulphate in the calcine must be operated at a lower temperature, especially on the lower hearths, than when roasting in the normal manner. A large amount of air must be admitted to the lower hearths, which gives a greater dust loss due to the increased gas volume.

Behavior of Impurities in Roasting.—Varying percentages of arsenic and antimony are eliminated in roasting zinc concentrates, as is illustrated in Table 1. The amount eliminated probably depends on the form in which they occur in the concentrate. Most zinc ores are quite low in these impurities, which is indeed fortunate as they are among the most detrimental to the process.

Some copper combines with iron during roasting, the combination being insoluble in dilute sulphuric acid. Concentrates containing high percentages of iron produce a smaller proportion of soluble copper than those low in iron. Some copper sulphate is formed on the upper hearths of the furnace, but is later decomposed by the higher temperature on the lower hearths.

A large percentage of the lead content of the concentrate may be volatilized if the temperature of the upper hearths is too high. Too high a temperature in the furnace also may cause the lead to fuse and coat a considerable portion of the unroasted zinc sulphide, preventing further roasting of the coated particle. Some of the fused lead may also work into the hearth bed, forming a hard crust.

One disadvantage of the sulphate roast is the high percentage of soluble iron in the calcine. This would indicate that some iron sulphate is formed in roasting. In roasting without the necessity of forming sulphates, the finishing temperature is high enough to break up the iron sulphate, and most of the iron in the calcine is then insoluble in the leaching solution. All iron that is dissolved in the leaching solution is finally precipitated from solution as ferric hydrate or basic sulphate and, when too much is present, will render the residue from the leaching plant practically impervious to the passage of wash water.

Silver is rendered less soluble at low than at high temperatures; but when the initial roasting temperature is high, the silver is apt to be volatilized.

Chlorine and fluorine, if present, are largely eliminated during roasting, as most chlorides and fluorides are volatile at the temperature of roasting.

Notes on Roasting.—The bedding of calcine between the rakes and the brick hearths is found to contain a high percentage of zinc sulphate, especially on the second, third, and fourth hearths. This material becomes quite hard; the hardness increases with the temperature of roasting. At frequent intervals the rakes are removed from a rabble arm, a plow is put on, and the crust is cut loose from the hearth. This crust is then removed through the furnace doors. If allowed to stand in the open, this crust will absorb moisture and disintegrate. Usually this crust is crushed, ground, and returned to the furnace to be given additional roasting. In order to prevent the formation of heavy crusts, a layer of sand is spread over the brickwork

of the hearth before the furnace is started. This sand is renewed at intervals of about two years thereafter.

Some lumps are always formed during roasting and should be removed from the calcine before delivery to the leaching plant. If Pachuca tanks are to be used for leaching, the calcine must be screened through ⅛-in. screens. The oversize product usually contains enough sulphide sulphur to cause trouble in leaching, especially in cases where high acid strengths are used. When sulphide sulphur is present, a reduction of iron in solution from the ferric to ferrous state may take place with an increase in the loss of zinc in the residue. The oversize material screened from the calcine is crushed, ground, and returned to the furnace for further treatment.

The hot calcine from the roasters must be cooled in order to prevent injury to employees and to lessen the hazards from fire. In the Anaconda plants the processes of cooling and screening are carried out together. The hot calcine from the roasting furnace is conveyed by larry cars to bins above the coolers. These coolers are horizontal rotating cylinders, lined with a large number of pipes. Cooling water is circulated through the pipes; and the calcine is cooled during passage through the cylinders. The calcine when reaching the discharge end of each cooler is passed over a ⅛-in. trommel screen rotated by the cooler. The undersize material drops through the screen into storage bins directly beneath. The oversize falls into a screen conveyer where it is carried to a vibrating screen where further classification is made. The large lumps that will not pass through a ⅜-in. screen are collected, crushed, ground in a ball mill, and returned to the roasters. The lumps that pass a ⅜-in. screen but not a ⅛-in. screen are ground in a ball mill, without crushing, and also returned to the roasters. The material passing through the ⅛-in. screen is regular calcine and is suitable for delivery to the leaching plant.

PRODUCTION OF A PURE ZINC SOLUTION

Classification of Operations.—The operations necessary for the production of a pure zinc solution from roasted zinc concentrates fall into two main types: leaching and purification. Theoretically, leaching should be concerned only with the dissolving of zinc oxide and sulphate; but, from the economic standpoint, it must also include the treatment of zinc ferrites and other difficultly soluble compounds. A leaching process strenuous enough to dissolve certain zinc compounds may take other elements into solution, thus making the purification process much more complicated. The purification processes, under these conditions, fall into three main classifications: ferric hydroxide purifications, zinc-dust precipitations, and special chemical purifications.

Chemically, the leaching and purifying processes are separate and distinct, but in commercial practice they are sometimes so interwoven that division is difficult. Much of the actual purification of solution takes place in the leaching tanks. The dissolving of zinc oxide, for example, is often simultaneous with the removal of certain impurities by ferric hydroxide in a single neutral leach.

Equipment.—Standard types of leaching, settling, filtration, and clarification equipment have been adapted to the needs of the process, thereby simplifying the mechanical problems. Pachuca tanks are generally used for leaching, the size depending on the needs of the plant; standard thickeners are used for thickening of pulp; standard continuous vacuum filters are employed for filtration of the thickened pulp; any type of mechanical agitator of large capacity will answer for zinc-dust purification; and standard pressure filters are used for clarification of solution. All equipment should be constructed of materials not attacked by acid or by copper in solution. Lead and wood are commonly used for the construction of parts in contact with acid, and lead, copper, or bronze for parts in contact with neutral solutions containing copper. The recent developments in alloys have produced materials that are rapidly

being adopted by the electrolytic-zinc industry. A further increase in the use of these materials can be expected as their production is increased and their applications are proved.

The use of materials that are resistant to corrosion requires considerable extra capital outlay over the cost of similar equipment of iron and steel. This is largely offset by the high salvage or scrap value that can be credited against the heavy first cost of construction.

The Pachuca tank is especially well adapted to the continuous leaching practice that has been adopted by the larger plants. The Pachuca tank operates on the same principle as the common air lift. Pulp is circulated and agitated by means of an air lift placed centrally in the tank, the pulp entering the lift at the bottom of the tank and being discharged at the top. The common size of tank is 8 to 10 ft. in diameter and 20 to 30 ft. deep. An inverted cone built into the bottom of the tank serves to deflect solid particles to the center so that they will be drawn into the air lift. The tank and air lift are made of wood, and the tank staves are bound together with iron hoops covered with sheet lead. An extra lining of wood inside the tank serves as a protection to the tank staves and can be easily renewed when necessary. This adds materially to the over-all life of the tank proper. Figure 4 shows the usual form of a Pachuca tank, with the method of supporting the central air lift and of admitting the air to the lift.

Compressed air at 20 to 30 lb. pressure is employed for agitation of the pulp. The consumption of air ranges from 100 to 150 cu. ft. of free air per tank per minute in order to maintain sufficiently violent agitation to prevent classification of the pulp. Even then some classification takes place, and over a long period of time the tank begins to build up in solid particles too heavy to be moved by normal agitation. It is advisable that the air supply to the tanks be also connected to a source of air under 80 to 90 lb. pressure. Then, when a tank begins to load up in the bottom with heavy material, a short period of more violent agitation will usually clear it.

The tanks in continuous-leaching practice are in series with connecting launders at the top of the tanks. The rate of flow through the series of tanks may be regulated by partially closing the connections between tanks. The number of tanks in series depends on the volume of pulp to be handled per unit of time and the length of time required to complete the reactions.

The leached pulp going to the neutral thickeners sometimes contains such a large amount of coarse material or "sand" that, unless removed, it would cause trouble with the thickener mechanism. If this is the case, the pulp is first passed through some type of classifier or sand trap and the coarse particles are removed. The trapped "sand" is then either added to the thickener underflow or given special treatment.

Standard thickeners are used for the separation of solution and solids. These are much the same type as those used in cyanide practice; but more slope and a larger discharge cone for the thickened pulp should be provided, especially for thickeners handling an acid product. The tanks are made of wood staves held together with iron hoops covered with sheet lead. The bottoms of the thickeners are often made of concrete poured over sand on a wooden floor. Overflow launders are made of wood. They may be lined either with brick or with a thin layer of wood that can be easily replaced when worn. Launders for use with acid-bearing solutions are often lined with sheet lead.

The drums or forms of the continuous vacuum filters used are made of wood or bronze, and the tanks are of either wood or steel with a lead lining. All pipes and fittings are of copper or bronze. For the filtration of a slightly acid pulp, the best filter cover yet developed is a pure unwashed wool blanket, placed so that the nap is on the outside of the filter. Such a cover will not "blind" easily, as the threads do

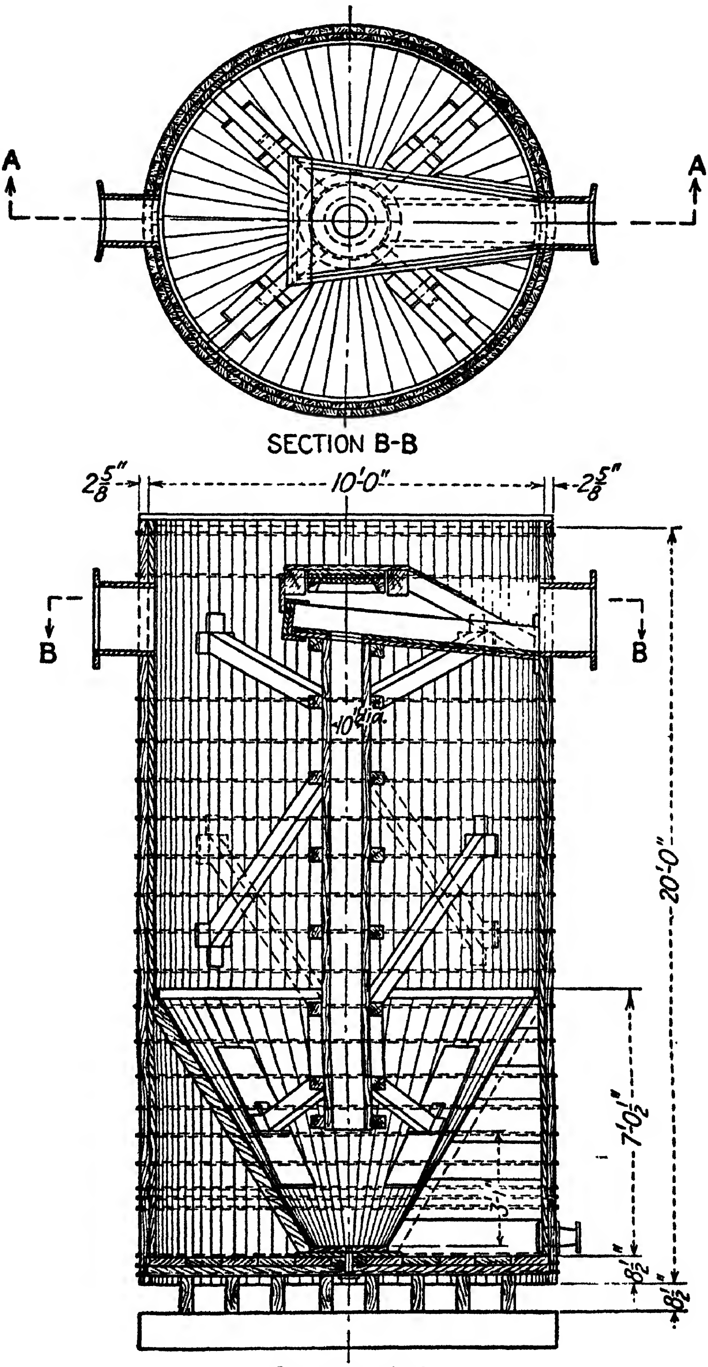

Fig. 4.—Pachuca tank for zinc leaching.

not swell when soaked in dilute acid. Also the nap acts as an automatic valve, closing when under suction and opening and freeing the cloth when under pressure. The natural oil in the wool protects the fiber against attack of dilute sulphuric acid. The dry vacuum system is used, and the solution receiver is made of either wood or bronze. To prevent vapor or spray from getting into the vacuum pumps and corroding valves and cylinders, receivers and traps should be of extra-large capacity.

Mechanical agitators with bronze or wood shafts and impellers are used for zinc-dust purification of solution. Plate-and-frame filter presses of bronze are generally used for clarifying the solution. Zinc sulphate solution, even when free of copper, will cause iron plates to corrode quickly, thereby plugging solution passages. All pumps and solution lines for handling neutral solutions containing any copper are made of bronze, copper, or stainless steel. Lead or stainless steel pumps are used for acid solutions, while wood or lead lines are used for conveying the solution.

Leaching.—The primary object of leaching is to dissolve all zinc oxide and zinc sulphate contained in the roasted concentrate in dilute sulphuric acid according to the reaction of $ZnO + H_2SO_4 = ZnSO_4 + H_2O$. Unfortunately, some iron, arsenic, antimony, silica, alumina, copper, cadmium, cobalt, germanium, and a few other elements are also dissolved and must be removed from solution before successful electrolysis can be carried out. It is necessary to neutralize completely all sulphuric acid to ensure the removal of most of these impurities. This may be done as a continuation of the leaching operation by the addition of finely ground limestone or milk of lime. This constitutes what is known as "single" leaching. It is not possible to neutralize exactly all free sulphuric acid and precipitate the necessary impurities by the addition of calcine. Excess calcine is required to complete the reactions, resulting in a serious loss of zinc in the residue and undissolved zinc oxide. In order to allow the use of calcine for neutralization and precipitation of impurities, without impairment of zinc recovery, a leaching system is employed whereby the residue from the first or neutralizing leach is treated with an excess of dilute sulphuric acid to dissolve all acid-soluble zinc. This system of leaching is known as "double" leaching.

"Single" leaching may be conducted as either a continuous or intermittent operation, but is more easily controlled if the intermittent or "batch" system is used. Calcine is added to regenerated acid from the electrolyzing cells until the acid strength is reduced to as low a figure as possible without impairing the satisfactory recovery of zinc—0.3 to 0.5 per cent H_2SO_4. Limestone, finely ground, or milk of lime is then added in sufficient amounts to neutralize the remaining acid. Enough excess must be added to precipitate all the iron, silica, alumina, arsenic, and antimony present and to coagulate the pulp so that good settlement of the residue and a clear thickener overflow is obtained. A great deal of care must be taken by the operator in the single leaching system in order to get a satisfactory extraction of zinc. Only enough calcine should be added to bring the acid strength down to the desired point after a long period of agitation, as any excess over this amount will result in a loss of zinc. Milk of lime and, to a less degree, limestone will precipitate zinc from a neutral zinc sulphate solution, causing some loss of zinc. All the acid neutralized by limestone or milk of lime must be replaced either by the addition of fresh acid or by increasing the amount of zinc sulphate formed during roasting. The calcium sulphate formed by the use of limestone or milk of lime increases the bulk and moisture content of the residue. These materials when used are also quite an additional expense in the supply account. Normally, the only justification for the use of single leaching with dilute sulphuric acid is the saving in the cost of plant and in the operating cost. Only a single set of tanks and thickeners, with the necessary auxiliary equipment such as classifiers, pumps, etc., is required for the application of this method of leaching. A plant producing only a small daily tonnage of zinc, requiring a small volume of solution,

should use intermittent or batch leaching for the first or "neutral" leach, thereby saving enough in first cost for building and leaching equipment to offset any additional operating cost.

The single leaching process as practiced by the Sullivan Mining Co., at Kellogg, Idaho, makes use of lead-lined mechanically agitated tanks. No limestone or milk

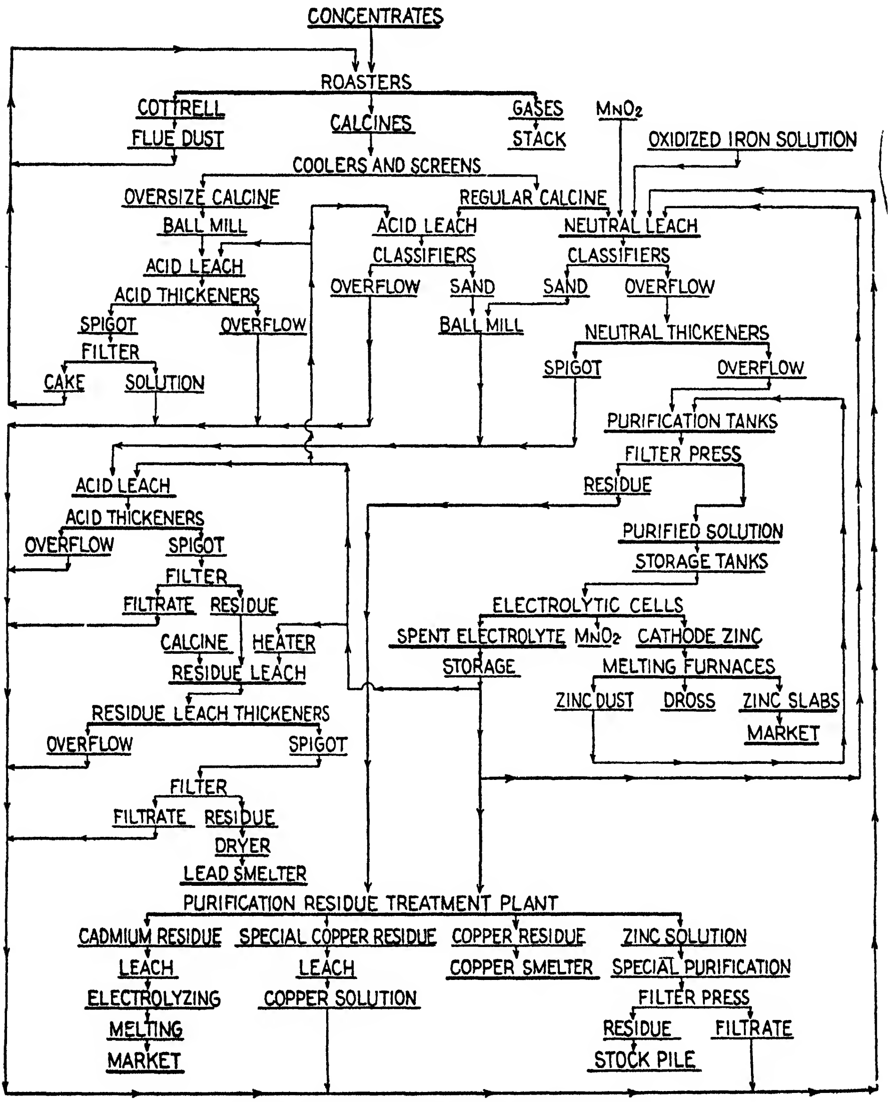

Fig. 5.—Flow sheet, Great Falls zinc plant.

of lime is used to finish neutralizing the last of the acid, but a reacidification process is employed. The first portion of calcine is leached at a minimum of 4 to 6 per cent acid. The remaining acid is then neutralized with small portions of calcine accurately measured. The leach is then reacidified to 2 to 3 per cent acid by the addition of more acid. Calcine is again added in small amounts. Any excess over the amount

necessary to neutralize the acid and to precipitate nearly all the iron is avoided. This method of making the leach improves filtration of the pulp. The Kellogg plant operates the high-acid high-current-density process, and the particular problems encountered do not generally apply to the low-acid low-current-density process.

The presence of a large amount of soluble silica in the calcine treated by the plant of the Electrolytic Zinc Co. at Risdon, Tasmania, resulted in the development of a single leaching process particularly suited to the character of the material. The leach is maintained acid, and instead of neutralizing the acid immediately, this step is not carried out until most of the insoluble residue is separated from the solution. In the usual manner of neutral leaching the problems of filtering, washing, and drying caused serious difficulties because of the large amount of silica present. The present system was worked out to surmount these problems.

Double leaching may be conducted as either a continuous or intermittent operation, but its most economical application is to a continuous-leaching system when there is a large volume of pulp to be handled. The Anaconda Copper Mining Co. plants at Great Falls and Anaconda, the Consolidated Mining and Smelting Co. plant at Trail, B. C., and the plant of the Hudson Bay Mining and Smelting Co. at Flin Flon, Manitoba, are among the larger producers using the double leaching system.

With the double-leaching system, the usual practice is to add all the calcine to a part of the acid (spent electrolyte) in the first or neutral leach. This gives a large excess of zinc oxide for complete neutralization of acid, removal of certain impurities, and coagulation of pulp. The discharge from this leach goes to thickeners for the separation of solids and solution. The spigot product from these thickeners, containing the incompletely leached solids, is then leached, with or without filtration prior to leaching, with enough spent electrolyte to dissolve all zinc oxide and to make the pulp distinctly acid—0.3 to 0.5 per cent H_2SO_4. The discharge from the second, or acid, leach goes to a second set of thickeners for separation of solids and solution. The solution from these thickeners is returned to the first leach and mixed with spent electrolyte to form the first leaching solution.

If the calcine does not contain sufficient soluble iron to remove completely all soluble arsenic and antimony, ferrous or ferric sulphate solution is added to the solution in the first leach. This iron solution is obtained either by dissolving scrap iron or by leaching some iron-bearing material with hot spent electrolyte. If ferrous sulphate is added to the first leaching solution, it is oxidized with manganese dioxide before the addition of calcine. Enough manganese dioxide is also added to the leaching solution to oxidize all ferrous iron dissolved from the calcine. The chemical equations involved are

$$2FeSO_4 + 2H_2SO_4 + MnO_2 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O$$
$$Fe_2(SO_4)_3 + 3ZnO + 3H_2O = 2Fe(OH)_3 + 3ZnSO_4$$

These reactions show that all sulphuric acid combined with the iron is eventually available to dissolve zinc oxide and that the iron is precipitated as ferric hydroxide, which is insoluble in neutral solution.

The formation and precipitation of ferric hydroxide assists in the removal of certain impurities, such as arsenic and antimony, from solution. This purification is very often explained as being due to the reaction of ferric hydroxide with the impurities to form insoluble basic salts according to the equation $4Fe(OH)_3 + H_3AsO_3 = Fe_4O_8(OH)_5As + 5H_2O$. Many authorities disagree with this theory and believe that the removal of impurities is due only to an adsorption process. Either theory has considerable evidence in its favor. Regardless of how the action takes place, it is sufficient to know that if enough iron is present, and the iron is all precipitated, these

elements are completely removed from solution. At least 10 units of iron for each unit of impurity is necessary for complete elimination.

The first leach is so controlled that a large excess of zinc oxide, over that necessary to neutralize the acid and to precipitate the iron, remains in the pulp. This hastens the precipitation of silica, alumina, iron, etc., and causes soluble silica to precipitate in a somewhat granular form. The pulp under these conditions settles readily in the thickeners. Heat also aids these reactions, and the higher the temperature, the more complete the purification of solution and the better the coagulation of the pulp. As this is usually the only purification step for arsenic and antimony, the leach must be so controlled that it is known positively at all times that this purification is complete. A simple method has been adopted for detecting the merest traces of arsenic and antimony in solution. A hydrogen generator using pure zinc and sulphuric acid is set up. The gas generated is passed through lead acetate solution to remove any traces of hydrogen sulphide, and then through silver nitrate solution. The solution to be tested is added to the hydrogen generator, and the silver nitrate solution is watched for a change in color. A trace of arsenic will give a brown discoloration and larger amounts will form a black precipitate.

Samples of the leach discharge are taken at regular intervals and tested for ferrous and total iron, arsenic and antimony, and copper. The test for iron is by titration with potassium permanganate, or it can be roughly determined with potassium sulphocyanate. The test is made by first adding a few drops of nitric acid to the sample to oxidize any ferrous iron present. Then the addition of a few drops of potassium sulphocyanate will indicate the amount of iron present by the depth of red color produced.

The recovery of zinc in the first, or neutral, leach is low, usually not over 60 per cent of the acid-soluble zinc being extracted. This is because of the large excess of zinc oxide necessary for complete precipitation of impurities. This necessitates the addition of about one-half of the spent electrolyte to the second, or acid, leach. If the neutral-thickener underflow product is not filtered ahead of the acid, a large quantity of neutral solution is recirculated through the system. This increases greatly the volume of acid-thickener overflow and dilutes the acid strength of the neutral leach to about one-third that of the spent electrolyte. This circulation of neutral solution has no particular disadvantage except for the number of acid thickeners and pumps required to handle the solution.

The object of the second, or acid, leach is to recover as much of the acid-soluble zinc as possible and the least quantity of impurities, as any impurities dissolved must be returned to the first leach. Spent electrolyte is added to the thickened or filtered neutral pulp in sufficient quantity to insure the presence of excess acid in the leach discharge. The amount of excess acid added largely determines the amount of impurities dissolved. If sufficient time is given for the leaching operation, practically all the acid-soluble zinc and only a small part of the total impurities will be leached with an acid strength of 0 5 per cent in the leach discharge. Figure 6 illustrates graphically the behavior of some of the soluble impurities in the first and second leaches. Some of the impurities dissolved in the second leach are derived from the excess calcine added in the first leach. If the acid strength is carried as high in the second leach as in the first leach, more impurities will be dissolved because there is much less zinc oxide present to neutralize the acid. If most of the zinc oxide is dissolved while there is still an appreciable amount of acid present in the leaching solution, the acid then has a greater opportunity to act on the more insoluble impurities. Until all iron, arsenic, antimony, etc., soluble in an acid solution of given strength is dissolved from the pulp, the acid-thickener overflow is a saturated solution of these impurities for that acid strength. With the volume of the solution constant, more or

less of these impurities will be dissolved if the acid strength is increased or decreased. An increased volume of solution at a given acid strength also increases the amount of impurities dissolved. Therefore, if either the volume or acid strength of acid-thickener overflow is increased, the amount of impurities circulated will increase up to the point where all these elements soluble in the existing acid strength have been dissolved. Also, if either or both the volume and acid strength is decreased, less impurities will be circulated. It is highly desirable to keep the volume of solution and the amount of impurities circulated at a minimum to facilitate settlement in both the neutral and acid thickeners. A decrease in the volume of solution circulated also slows down the flow of solution through the same amount of equipment and gives time for more complete leaching. A decrease in the volume of solution circulated can

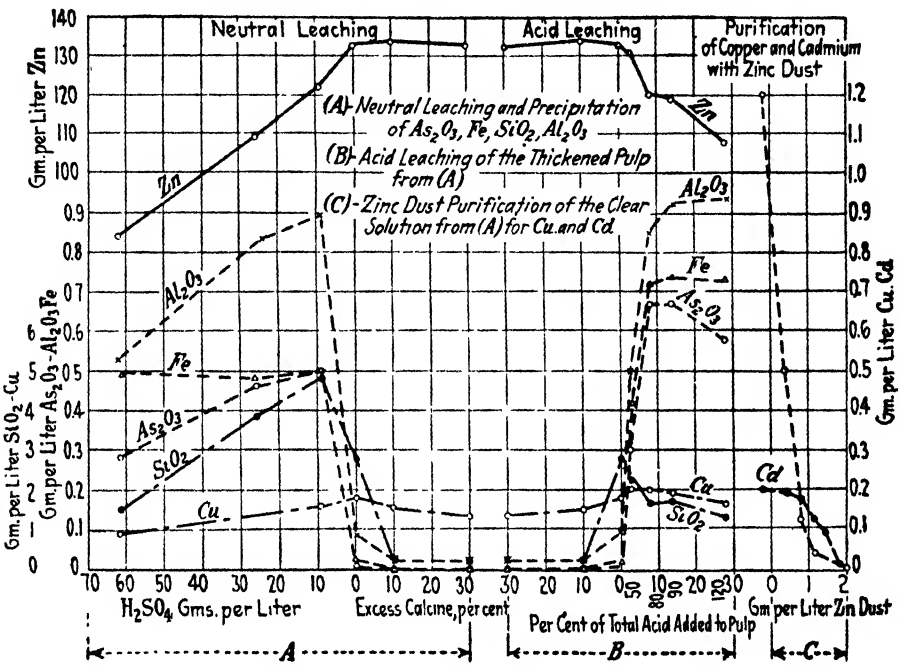

FIG. 6.— Behavior of soluble impurities.

best be accomplished by filtering the neutral-thickener spigot product ahead of the second leach. The filtered solution can then be added to the neutral-thickener overflow instead of circulating it through the leaching and settling system. Dissolving a larger amount of zinc in the first leach reduces the amount of solution required in the second leach, but carrying this too far is dangerous practice, as some excess zinc oxide is necessary for complete precipitation of impurities and for coagulation of the pulp.

The pulp from the acid leach does not settle as rapidly as properly coagulated neutral pulp. Some fine solid material always overflows the acid thickener and is put back into the neutral system. This constitutes an additional burden for this equipment. The amount circulated depends partly on the rate of flow through the thickeners. A reduction in the volume of solution passing through the acid system will, therefore, reduce the amount of solids as well as the amount of impurities returned to the neutral system.

An apparently simpler method of accomplishing the desired results from the double-leaching system would be to treat all the spent electrolyte with enough calcine to reduce the acid content of the leaching solution to about the same strength as the acid-thickener overflow—0.3 to 0.5 per cent H_2SO_4—and then to neutralize and purify the resulting solution with excess calcine or limestone as a separate step. In this method, if calcine is used, the residue is returned to the leaching system, or if limestone is used, the residue is discarded. This method of leaching dissolves more impurities from the calcine because of the high acid strength of the leach. The residue from a leach of this type settles very slowly and is difficult to filter. Precipitated hydroxides and gelatinous silica require the weight of the main body of the residue to carry them down in the thickeners. They also filter much more readily when mixed with the sandy portion of the residue.

"Continuous" vs. "Batch" Leaching.—The continuous-leaching system is well adapted to plants handling a large volume of solution and having a fairly uniform feed. The main disadvantage of the continuous-leaching system is that sudden changes in the analyses of feed make a close control of the purification part of the leach almost impossible. It is therefore necessary that a continuous-leaching system be operated at all times under conditions suited to the maximum amount of impurities that might be encountered. This is the only positive way to ensure that no improperly purified solution will get by to the electrolyzing cells. With a batch-leaching system, each tank of solution can be held until its purity is assured. A larger proportion of the zinc content of the calcine can be recovered in the neutral leach with the batch system, as more time can be allowed for the addition of calcine and for agitation between additions. A much closer control can also be had of the amount of calcine added in excess of that necessary for neutralization. This results in less acid-thickener overflow returning to the neutral leach and improves conditions generally in the acid leach.

Air consumption is greater with the continuous-leaching system than with the batch system for a small plant. This is because it is necessary to maintain agitation in all the tanks continuously to prevent settling of the pulp, which would plug the air lifts. With the batch system each tank is completely emptied at the end of each leach, and air is used only during the actual period of leaching. A plant producing 50 tons of zinc per day, even with a low-acid process, will require less than 1000 tons of solution per 24 hr. This amount of solution can be handled more economically and with better leaching results in the same number of tanks operating independently than if arranged in series. As the volume of solution increases beyond the capacity, if operated independently, of the minimum number of tanks that can be placed in series for successful continuous leaching, then the comparison changes in favor of continuous leaching, owing to the saving in time required for filling and discharging.

Labor and repair charges are lower with continuous leaching, and the entire leaching operation is simplified. The capacity per tank is greater, giving fewer units for leaching and for calcine storage. Also, less difference in elevation is required between leaching tanks and thickeners, when gravity feed is used, owing to the fact that the tanks are discharged from the top instead of the bottom.

In general, plants of small capacity and those having a very variable feed are best served by the batch system, and those of large capacity and having uniform feed are best served by the continuous system for the neutral leach. For the acid leach the continuous system is preferable for all plants.

Purification of Neutral Solution.—Neutral-thickener overflow will be free of iron, arsenic, antimony, tin, bismuth, and silica, if the neutral leach has been properly carried out. The overflow will, however, contain 40 to 60 per cent of the copper and most of the cadmium originally present in the calcine. These two are usually the major impurities, but germanium, nickel, cobalt, etc., will also be found in the solution

if these elements were in the calcine to any extent. Some of these impurities have an adverse effect on ampere efficiency and must be removed to avoid trouble during electrolysis. Others are plated out with zinc and must be removed from solution previous to electrolysis if a pure zinc metal is desired. Both types of impurities are usually removed from neutral-thickener solution by mechanical agitation with finely divided zinc dust. The process of purification is usually so complex that adequate control cannot be obtained by continuous purification systems. Mechanical agitation is preferred to air agitation because of the tendency of certain impurities to oxidize and redissolve on contact with air. A single zinc-dust treatment will sometimes remove all undesirable impurities from solution, but often the purification must be divided into two or more "stages," each with its individual precipitation and filtration. An excess of zinc dust over the theoretical replacement amount is usually necessary to effect complete precipitation of impurities. Most of this excess zinc can be recovered from the purification residue and does not constitute a loss. The extent and intensity to which purification must be carried out, and the exact manner in which it is performed, depends on the particular impurities present, their relative amounts, and the degree of purity desired in the metal produced.

Copper and cadmium are the two harmful impurities usually found in relatively large amounts in the neutral-thickener overflow. If they are the only impurities present, both are easily removed by a purification with zinc dust. Copper precipitates first and has no tendency to go back into solution. Cadmium removal is not so complete; an excess of zinc dust above the theoretical replacement amount is necessary for adequate purification. The precipitation of cadmium is partially dependent on the copper content of the solution. A small amount of copper assists in cadmium removal; but if the ratio of copper to cadmium is high, the freshly precipitated cadmium tends to redissolve, and an even greater excess of zinc dust must be used.

Copper and cadmium are seldom the only harmful impurities found in neutral-thickener overflow. The presence of copper is beneficial in removing these other impurities, and if sufficient copper is present, most of them can be eliminated in the same zinc-dust purification that removes copper and cadmium. If not enough copper is originally present to make the purification sufficiently strenuous, it can be supplied by the addition of copper sulphate solution. The presence of other impurities and the addition of copper to remove them increase the tendency of cadmium to redissolve. In many instances the re-solution of cadmium is so great that a second zinc-dust purification must be made. This is especially true if high-grade zinc is to be produced. In this case the first treatment with zinc dust precipitates all the copper in solution, together with most of the cadmium and other impurities. The purification residue is filtered off, and more zinc dust is added to the clear solution. This second purification completes the removal of cadmium. It is sometimes made more effective by the addition of a small amount of dissolved copper, usually less than 0.1 g. per l.

Arsenic and antimony are often present in neutral-thickener overflow in small amounts, although, theoretically, the iron-hydroxide precipitation in the neutral leach should completely remove them from solution. The zinc-dust purification is very effective in removing these two impurities if enough copper is present.

Antimony may be present in some ores in sufficient quantities to complicate the usual neutral-leach purification. This condition is rarely met, but was encountered in the treatment of fume from the Mammoth smeltery at Kennet, Calif. Purification of solution in this case was accomplished by precipitating arsenic, antimony, copper, and cadmium with hydrogen sulphide gas. The neutral solution was acidified to 0.5 to 1.0 per cent acid and treated with H_2S gas. This method has received little favor from the industry for several reasons: it is difficult to remove the last traces of antimony in this manner within a reasonable length of time without the use of an

enormous amount of equipment, hydrogen sulphide is both obnoxious and poisonous and requires special care and equipment for application on a large scale, and settling and filtration of precipitated antimony are difficult, due to the extreme fineness of the particles.

Silica, if not removed from solution in the neutral leach, is precipitated by zinc dust. This increases the amount of zinc dust required and impairs subsequent filtration by "blinding" the filter medium. An excessive amount of silica tends to form a gelatinous coating around each particle of zinc dust; in extreme cases this action is so great as totally to prevent further purification. This condition requires special treatment to be given in the neutral leach to reduce the amount of silica in the neutral solution. Solids overflowing the neutral thickeners, because of poor settlement, will also raise the consumption of zinc dust and increase the burden on the clarification filters. In order to obtain the slightest efficiency from the zinc dust used, the solution to be purified must be free from mechanically held solids and from such soluble impurities as silica, ferric sulphate, and free acid. Ferric sulphate and free acid will dissolve precipitated cadmium and increase the consumption of zinc dust. Filtration of the neutral-thickener overflow is sometimes resorted to in order to obtain a solution absolutely free of solids.

The discharge from the purification tanks is either filtered direct in a pressure filter to remove the purification sludge, or is first sent to settling tanks to take some of the load of solids from the filters. While settling relieves some of the load, it also increases the possibility of cadmium becoming oxidized and "riding back." Filtration at this point must be perfect, and the filtered solution should be crystal clear. Any solids going through the filter medium are certain to cause trouble later in the electrolyzing cells. If the solid particles are copper or cadmium sludge, they will be dissolved by the acid in the cells and impair either the ampere efficiency or the quality of the metal produced, or both; if the solids are particles of residue overflowing the neutral thickeners, arsenic and antimony will be dissolved in the cells. Settling alone is not sufficient to ensure the necessary clarity of solution. The solids from the purification step are treated in a separate leaching cycle for the recovery of zinc, copper, and cadmium.

Filtration of Residue.—The most serious problem in the filtration of residue is to avoid the loss of zinc as entrained solution in the final material. Pulp that is slightly acid is especially difficult to handle. The gelatinous precipitates of iron and aluminum hydroxide and silica form a cake more or less impervious to the passage of wash water. The residue from a low-grade concentrate contains a rather high proportion of sandy material and can be washed with sprays. As the zinc content of the concentrate increases, the proportion of gelatinous to sandy material increases and washing becomes more and more difficult. Finally a point is reached where sprays cannot be used satisfactorily and washing must be done by dilution. A normal residue filter cake from a concentrate containing 30 to 35 per cent zinc will contain about 25 per cent moisture, while a residue from a concentrate containing 55 per cent zinc will carry 35 per cent moisture or more.

Washing by replacement is more efficient, less expensive, and requires less water than washing by dilution. In either type of washing, hot water is more efficient than cold. The viscosity of zinc sulphate solution increases with a decrease in temperature, and as the viscosity increases, it is less readily miscible with water. Heating the pulp to be filtered increases the capacity of a filter owing to freer passage of solution and also decreases the moisture content of the filter cake. The amount and method of washing are partly governed by the zinc content of the solution in the pulp being filtered. As the zinc content of the solution increases, the loss of water-soluble zinc increases, unless additional washing is provided.

A combination of washing and replacement and dilution is generally used when treating a residue from low-grade concentrates. Spray washing is used first, the resulting cake is repulped with hot water in a suitable agitator, and the resulting pulp is refiltered on a second filter on which spray washing is used. Repulping may be done in several types of agitators, but an adaption of a pugmill is one of the simplest and cheapest devices. A trough is fastened to the cake-discharge side of the filter to receive the cake as discharged. In this trough is a revolving shaft carrying pugmill blades and driven from the filter mechanism. Water is added to the trough in sufficient quantity to form a pulp of the proper density and after being mixed with the cake is discharged to a second filter. The amount of wash water that can be used is limited by the moisture carried out in the residue and the evaporation throughout the plant, unless some solution is discarded for other reasons. Pulp fed to the filters should be sufficiently thick to prevent much classification in the filter tank, or the sandy material will settle in the tank, and the filter cloth will become "blinded" with slime.

Washing a residue produced by high-grade concentrates presents a somewhat different problem. Here the pulp contains a relatively low percentage of sandy material, and washing with sprays is not practical. Repulping this residue results in a frothy sticky mass which is difficult to filter and retains a large amount of moisture. Even handling this pulp through a centrifugal pump increases its resistance to filtration. This pulp is usually handled in some type of filter, such as a Moore filter, in which washing is done by replacement. This step is then followed by a second filtration in which the pulp is dewatered as much as possible.

Vacuum used should be maintained as high as possible in order to reduce the moisture in the cake to a minimum and to keep the capacity of the filter at a maximum. The dry-vacuum system is much to be preferred, but must be provided with large solution receivers and moisture traps to avoid carrying solution or spray into the vacuum pumps. A slight leakage of solution or spray will soon corrode the valves and cylinders of the pumps to a point where they lose efficiency and will in a short time cause more serious trouble through breaking of valves and pistons. Traps and receivers made of wood staves are preferable to steel tanks with lead linings. Lead linings tend to collapse and break along the seams, giving the solution a chance to corrode the tank shell, and for this reason are expensive to maintain. Bronze or copper may be used in many cases but are expensive to install.

Recovery of Zinc from Residue.—The residue from the treatment of any concentrate containing iron will contain some undissolved zinc in the form of zinc ferrite. The residue will also contain any unroasted zinc sulphide introduced with the calcine, some zinc sulphate as entrained solution, and some undissolved zinc oxide in the small lumps that have not been penetrated by the leaching solution. As a general rule, the higher the zinc content of the concentrate, the smaller the percentage of the total zinc that remains in the residue. With a high-grade concentrate, a smaller percentage of zinc ferrite is usually formed during roasting because of the better separation of iron and zinc during the concentrating process, and because the iron and zinc are normally not in as intimate contact as in a low-zinc high-iron concentrate. Less sulphide sulphur remains in the calcine produced from a high-grade concentrate because of the higher roasting temperatures permissible in the absence of a relatively large amount of iron. The treatment of a concentrate containing a high percentage of zinc results in the formation of a smaller amount of insoluble zinc compounds during roasting; the smaller amount of insoluble zinc compounds formed results in a smaller amount of residue; and the smaller amount of residue produced decreases the loss of zinc sulphate as entrained solution, and allows more wash water to be used per ton of residue.

The amount of special residue treatment necessary to obtain a good over-all recovery of zinc must first be considered from the economic standpoint. While the several methods often used to recover zinc from the residue may be metallurgically sound, they may not be practical if conditions are such that it is cheaper to buy new concentrate than to treat the residue.

Regardless of the percentage of the total zinc concentrate that is contained in the residue, the residue may contain enough zinc economically to warrant special methods of treatment for its recovery. On the other hand, the loss of zinc, per ton of concentrate, in the residue may be excessive, yet the zinc content, per ton of residue, may be too low to pay for the cost of treatment. For example, assume that two concentrates are under consideration. The first contains 60 per cent zinc from which a recovery of 95 per cent can be obtained and from which 0.2 tons of residue is produced per ton of concentrate. This residue will contain 15 per cent zinc. The second concentrate contains 30 per cent zinc from which a recovery of 80 per cent can be obtained, and 0.65 tons of residue is produced per ton of concentrate. The residue from this concentrate will contain 9.25 per cent zinc. The residue from the first concentrate is an attractive one to treat, while the other is so low in zinc that conditions would need to be especially favorable for the value of the zinc extracted to pay for the cost of treatment.

Zinc ferrite is practically insoluble under the usual leaching conditions, and unless special recovery methods are employed, the loss of zinc in the residue is likely to be serious. A great many methods have been investigated and proposed for the extraction of zinc ferrite, but only a few have been found to be commercially feasible. The loss of zinc in the residue as zinc oxide, zinc sulphide, or zinc sulphate is large enough to receive some attention, but if an effective method of recovering zinc from zinc ferrite is used, the zinc in these other compounds is largely recovered in the same process.

Roasting the residue in an atmosphere of SO_2 gas at a temperature of 500 to 550°C. will convert most of the zinc ferrite to zinc sulphate, which is soluble in water. Some iron sulphate is formed during the roasting, and unless the temperature is raised above 600°C., iron will be extracted with the zinc by water leaching. By a careful regulation of temperature during the roast, the solubility of iron can be controlled to any desired degree. The reaction causing the decomposition of ferrite and the sulphating of zinc is probably due to the action of SO_3 gas. Ferric hydroxide decomposes at the temperature of the roast to form ferric oxide, which acts as a catalyst in converting a mixture of SO_2 and O_2 to SO_3. The SO_3 so formed is then available for the sulphating reaction. This method was investigated during the early development of the zinc plant at Trail, B. C. The residue was treated in a multiple-hearth furnace, and pyrite was added to the lower hearths to furnish the SO_2 necessary for the decomposition of ferrite. This method was commercially successful for a time, but as the capacity of the plant increased, it was found to be rather slow for large-scale operations.

The "residue-fuming process" is another method used for the recovery of zinc from zinc-plant residue. This process depends on the decomposition of zinc ferrite and the formation of zinc sulphate when the residue is roasted with sulphuric acid at a high temperature. The reaction is probably carried out according to the equation: $ZnO.Fe_2O_3 + 4H_2SO_4 = ZnSO_4 + Fe_2(SO_4)_3 + 4H_2O$. The sulphates of zinc and iron formed by this reaction are both soluble in a water leach. Some soluble ferric sulphate may be desirable as a source of iron for the neutral leach. The amount of ferric sulphate remaining in the finished product can be controlled by regulating the temperature of the roast. If the temperature is maintained above 600, but below 650°C., the ferric sulphate is rapidly decomposed into insoluble ferric oxide while the zinc sulphate remains practically unchanged.

A high recovery of zinc can be obtained by this method—75 to 80 per cent of the zinc in the residue—but there are two serious difficulties to be overcome. Evaporation of spent electrolyte to the concentration necessary to ensure sulphating is not a simple problem because zinc sulphate is crystallized out as the concentration increases. The solution can be depleted to about 5 g. per l. zinc before evaporation, but only at the expense of ampere efficiency. If a cheap source of commercial sulphuric acid is available, it may be more economical to deplete part of the spent electrolyte of its zinc content and to discard enough of this solution to offset the addition of fresh acid, than it is to evaporate spent electrolyte by ordinary means. The second difficulty to be overcome is the handling and roasting of the mixture of residue and acid. If all the acid necessary for complete sulphation is added to the residue at the start, the resulting mixture is too thin to be handled in the usual types of large-scale drying equipment.

Treatment of Copper-cadmium Residue.—The residue produced by purification of solution with zinc dust contains too much excess zinc dust to be discarded, and usually carries sufficient cadmium to pay for the necessary treatment to recover this metal. The copper content of this residue can also be recovered. Some basic zinc sulphate precipitated during the purification and clarification operations will be found in the residue. Unless the neutral-thickener overflow is filtered previous to purification, some recoverable zinc from slimes will also be present. The zinc from all these sources is just about equal to the amount of zinc dust used in the purification operation. Treatment of the purification residue is, then, necessary from the zinc-recovery standpoint, and is also desirable because most of the copper and cadmium can be recovered.

Purification residue is leached with dilute sulphuric acid (spent electrolyte) to dissolve as much zinc and cadmium as possible. The residue may be treated in either the oxidized or unoxidized condition. Oxidation, either by roasting or by long exposure to air, increases the solubility of zinc and cadmium to some extent but also increases the solubility of copper. If the residue is treated before complete oxidation takes place, the probable formation of arsine must be taken into account.

Oxidized purification residue is usually leached by adding the residue to the spent electrolyte until all the acid is neutralized. When leached in this manner, most of the zinc and cadmium is dissolved, and also a considerable portion of the copper goes into solution. The remaining sponge copper and insoluble material is settled out in thickeners, and is a desirable product for treatment by copper smelters. The thickener overflow, containing zinc, cadmium, and copper, is then treated with just enough zinc dust to precipitate all but a very slight amount of the copper present. The sponge copper from this operation is a desirable source of copper for use in the regular leaching operations; or it can be added to the first copper residue. The solution after being purified for copper is then treated for removal of its cadmium content. This can be done either by agitating with zinc dust, or by circulating the solution through tanks in which zinc slabs are suspended. In the first case, the action is much faster and is very satisfactory if a certain amount of zinc in the cadmium sponge can be tolerated. A cadmium sponge of greater purity is obtained by the use of zinc slabs. Most of the cadmium sponge in this case floats to the top of the solution and is removed by skimming. The sponge cadmium can be used for the production of cadmium metal. The solution, after the cadmium is removed, is sent to the main leaching system. If this solution contains an appreciable amount of undesirable impurity, such as cobalt, it is good practice to remove the impurity before returning the solution to the leaching system. Cobalt can be removed by the use of nitroso-beta-naphthol if the iron in solution is first precipitated. If the cadmium content of the solution is low, cobalt can be removed by sodium-ethyl-xanthate without any preliminary treatment.

If purification residue is treated with dilute sulphuric acid before much oxidation takes place, most of the zinc and cadmium goes into solution, but only a small amount of the copper is dissolved. The presence of a certain amount of metallic zinc and cadmium at all times causes the immediate reprecipitation of most of the copper, nickel, or cobalt dissolved. Settling or filtering a leach made in this manner results in a copper residue and a zinc-cadmium solution practically free from harmful impurities. The cadmium in the solution is precipitated, and the subsequent operations are carried out in the same manner as when oxidized residue is leached.

Purification residue may contain some arsenic, due to imperfect purification in the neutral leach. If the metallics always present in the freshly precipitated residue are not completely oxidized, then the treatment with acid will generate hydrogen. Hydrogen, when evolved in the presence of arsenic compounds, combines with arsenic to form arsenic hydride, commonly called arsine. Arsine is an extremely poisonous gas. A very little arsine, breathed into the human system, will cause serious illness or even death. It is, therefore, absolutely necessary to provide every possible safeguard in an operation of this kind. The purification residue treatment plant should be in a separate well-ventilated building. The leaching tanks should be hooded and connected to an exhaust fan of ample capacity to maintain a constant vacuum in the tanks and hoods. Samples of air should be drawn from different parts of the plant and tested for the presence of arsine. These samples should be drawn from near the surface of the settling tanks and, as arsine is heavier than air, from the low spots on the floor of the building. The tendency for arsine to collect in the low places is a dangerous characteristic. Unless every precaution is taken, it may collect unnoticed until some disturbance in the atmosphere of the building distributes it and poisons every employee in the department. A continuous test for the presence of arsine can very easily be made on the air samples drawn from various parts of the building. The air is first passed through lead acetate solution, to remove any H_2S that might be present, and then through silver nitrate solution. The presence of arsine in the sample causes the silver nitrate solution to turn black.

ELECTROLYSIS OF ZINC SULPHATE SOLUTION

Purity of Solution.—When the leaching and purifying operations have been properly carried out, the zinc sulphate solution delivered to the electrolyzing cells is almost entirely free from impurities that may be injurious to their operation. The electrolyzing cell is extremely sensitive to those elements which are electronegative to zinc. So marked is the action of certain impurities that they may have a detrimental effect on the cell when present in amounts too small to be detected by the regular methods. The effects of some impurities can be minimized by a change in operating conditions or by the use of certain addition agents, such as glue; but the only absolute guarantee of satisfactory results is purity of solution.

Next in importance to purity of solution is the purity of electrodes and tank-lining material. Pure chemical lead, or lead-alloy, anodes should be used. If the tanks are lined with sheet lead, only the purest lead obtainable should be used for this purpose. Aluminum of the highest purity should be used for the cathodes. A great deal of care should also be taken that no impurities accidentally find their way into the cell.

With the essential details taken care of, the electrolytic cell will allow a reasonably wide variation in operating conditions—such as temperature, acidity, current density, etc.—without much change in ampere efficiency. These conditions must, however, be considered in the economic success of the process as they are quite important in their effects upon the voltage required, and thereby on the power requirement.

Power Equipment.—Power is normally the largest single item in the operating cost of an electrolytic-zinc plant. Direct-current electrical power is necessary for electrolysis; and, in most cases, it must be converted from the alternating current supplied to the plant. The power requirement of the zinc cell is so great that the smallest possible conversion loss amounts to an appreciable sum in the larger installations. The size of the plant and the equipment available are the determining factors in deciding upon the conversion machine to be used. The gradual growth of the large zinc plants and the electrical equipment available at the time of the original capital outlay have resulted in the use of some conversion units which, if the ultimate size of the plant had been known, might not otherwise have been used. The conversion machines in general use are motor-generator sets, rotary converters, and mercury-arc rectifiers. Motor-generator sets are widely used in the smaller plants or where the growth of the plant has been gradual. They have a conversion efficiency of 85 to 88 per cent. Rotary converters, having suitable voltage control, are more efficient than motor-generator sets. The conversion efficiency of a large rotary converter is generally above 92 per cent and may be as high as 94 per cent. The higher voltage of the rotary converter permits more cells to be connected in series and requires fewer units. Larger and fewer units require less attendance and less floor space, making both first cost and operating cost less. Grounding the neutral point of each circuit lessens the possibility of personal injury with the higher voltage of the rotary converter. In over 25 years of operation at Great Falls, not a single injury has resulted from the exposure of over 200 workers per day to operating voltages of 500 to 550 volts. Mercury-arc rectifiers have a slightly higher conversion efficiency than rotary converters when operated at higher voltages than usually encountered in zinc plants. A factor of 94.5 per cent is obtained by the Magdeburg Zinc Works at Magdeburg, Germany, by operating mercury-arc rectifiers at 750 to 850 volts on the d-c side. Mercury-arc rectifiers have been in use for a long time; but only recent developments have given them operating efficiencies satisfactory to the zinc industry. A wider use of this type of conversion machine in the electrolytic-zinc industry can be expected in the future.

Tanks.—The tanks used as electrolyzing cells are usually constructed of wood, concrete, or pitch concrete. Many materials have been tried in the search for the "perfect tank," but very few have been found to possess enough of the essential qualifications to warrant their general use. The ideal tank should be relatively low in cost and give a long period of service. It should be a nonconductor and impervious to dilute sulphuric acid under electrolyzing conditions. It should be capable of carrying not only the load of solution, but also the weight of electrodes and tank bars.

Wood tanks were the first to be used for several reasons. Their ease of construction and apparent low cost were attractive, but the main reason was that during the early development of the electrolytic-zinc industry no better material was available. Wood tanks must be lined with lead or rubber to prevent leakage and to resist the action of dilute sulphuric acid. The wood used must be heavily creosoted to prevent rotting or disintegration due to the action of acid. The tanks must be well reinforced with tie rods and plates to withstand the load of solution and electrical equipment. Wood tanks are gradually disappearing and are being replaced by tanks constructed of materials having more of the essential qualifications of the ideal tank.

Concrete tanks must be lined with some material resistant to the corrosive action of dilute sulphuric acid. Lead, sulphur sand, or rubber are often used. Concrete tanks have a longer life and greater strength than wood tanks, but the cost is greater. They must be cast in wood or steel forms and aged 15 to 20 days before being put into service. Concrete is very susceptible to disintegration when in contact with acid; any leak developing in the lead lining is detrimental to the life of the tanks. This

effect can be partially prevented if the tanks are painted or varnished before lining, and if weep holes are provided in the bottom of the tanks. Nevertheless, this is a serious defect of concrete and overshadows many of the advantages of its use as a tank material.

Pitch-concrete tanks are, theoretically, the nearest approach to the perfect tank so far developed. They are a mixture of pitch, asphalt, silica rock, and silica sand. Pitch concrete has been used in Europe for several years for the production of acid-proof sewer pipe, tile, and the like; but its application to large castings was developed by the Consolidated Mining and Smelting Co., at Trail, B. C. Tanks made of pitch concrete are cast in one piece in steel forms. Special equipment is necessary for heating and mixing the material. Reinforcing wire and rods are used in the same manner as in reinforced concrete. When correctly made, pitch concrete equals concrete under compression, exceeds concrete in tensile strength, and does not require lead lining. The tanks are, however, quite fragile, and extreme care is necessary to

Fig. 7.—Great Falls tank house.

prevent cracks either from mechanical shock or from strains set up during the cooling period. Cracks when formed are quite difficult to repair. Several plants are now testing these tanks, but a long period of trial will be necessary before deciding whether this is the tank to be used.

The size of tank required depends on the number and size of the electrodes and the spacing between electrodes—4-in. spacing from center to center of anodes is about the maximum. Some space must be provided below the lower edge of the electrodes for settlement of the manganese dioxide sludge deposited at the anode. The space between the electrodes and the tank sides must be large enough to avoid striking the tank lining when the electrodes are removed. Overflow spouts of lead, rubber, etc., fastened either to the tank or to the tank lining at the lower end of each tank, are used to remove the spent electrolyte. No provision is made for draining the tanks from the bottom; it has been found cheaper and more satisfactory to empty the tanks for cleaning with a pump.

Electrodes.—Rolled aluminum sheets, $\frac{3}{32}$ to $\frac{3}{16}$ in. thick and of the highest purity, are used for cathodes. Copper support bars are riveted to the aluminum sheet; or copper inserts are cast into an aluminum header, which is then welded to the

sheet. Aluminum bars riveted to the sheets have been substituted for copper bars, but as electrical contact between aluminum and aluminum is not particularly good, excessive heating resulted. Sheets thicker than $\frac{3}{16}$ in. have been tried, but the added weight is an objectionable feature in removing plates for stripping. Wood, rubber, or rubber-lined aluminum strips are usually placed on the vertical edges of the sheets to prevent zinc building up around the edges. This serves the double purpose of eliminating the sharp edges where "trees" might form during the electrolysis and of increasing the ease of stripping. At Risdon, no strips are used; grooves are cut in the sheets along each edge to weaken the zinc deposit at these points so that the zinc can be more easily removed.

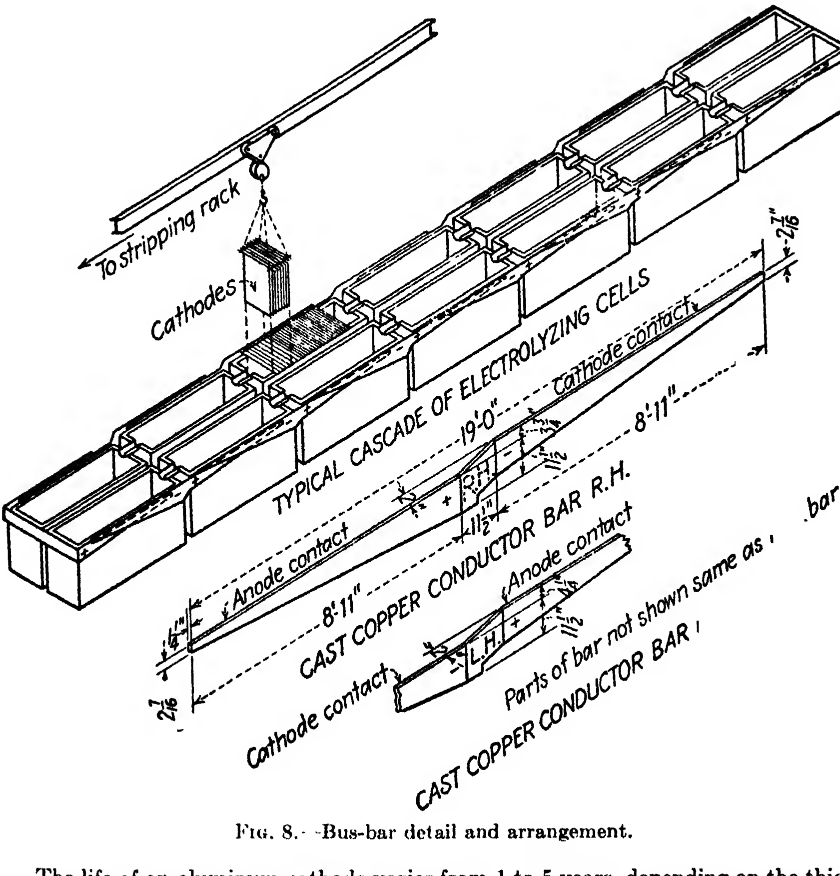

FIG. 8.—Bus-bar detail and arrangement.

The life of an aluminum cathode varies from 1 to 5 years, depending on the thickness of the sheet and the precautions taken to prevent corrosion. Most of the corrosion takes place just below the support bars. At the solution line, corrosion is considerably less, and below the solution line it is practically negligible. The life of the cathode can be greatly lengthened by using a sheet with a thicker cross section at the point of corrosion, or by riveting protecting plates of aluminum to the portion of the sheet above the solution line. The increased cost of fabrication and the high value of aluminum scrap have prevented the general adoption of the thickened cathode. The use of a paint or varnish that would stand up under chemical corrosion and mechanical wear would greatly prolong the life of the aluminum cathodes. Such a

paint or varnish has long been sought, but to date none of the many tested have proved commercially successful.

The anodes used in the zinc cell are of sheet lead 1/8 to 3/8 in. in thickness. Solid sheets are generally used, but perforated sheets are claimed to have some advantages. Where extremely close spacing of electrodes is practiced, some form of guide must be used to maintain this close spacing; and, because the circulation of solution is reduced by the guides, perforated anodes are almost a necessity. The anode sheets are usually cast, but rolled sheets may also be used. The anodes are generally cast around a copper header bar, leaving one end of the copper bar exposed to make contact with the tank bus bar.

Chemically pure lead, or an alloy of lead with silver, is used for the anode material.[1] Other alloying elements, such as cadmium, calcium, and arsenic, have been tested, but no element has been found to be as satisfactory as silver in preventing corrosion of the anode. Copper tends to build up in the lead when old anodes are melted and recast; it seems to have little effect on the anode in amounts up to 0.2 per cent.

The anode is the main source of lead in the cathode zinc, but the amount of lead plated out with the zinc is normally but a small part of the lead corroded from the anode. Most of the corroded lead remains as lead-manganese scale on the anode or settles to the bottom of the cell as a sludge. Both scale and sludge must be removed at regular intervals if the ampere efficiency of the cell is to be maintained, and if the lead in the cathode zinc is to be kept at a low level.

The length of time that an anode is used depends not only on the amount of corrosion of the lead, but also on the influence of the anode on the character and efficiency of zinc deposition. After a certain period of time, depending on local conditions, there is a gradual decrease in current efficiency and an increase in the amount of lead in the cathode zinc over that obtained with new anodes. When the optimum life of an anode has been passed, the anode is removed from the cell, melted, and recast. Some lead is lost during the melting as lead dross and must be replaced with new lead.

The size of the electrodes and the number used per cell depend on the capacity of the plant, the current density used, and other local conditions. Larger electrodes are required if the bus bars are carried on the edges of the tanks than if the bus bars are supported independently. This is due to the greater distance between the solution level and the electrode support bars. Spacing between electrodes in the cells varies from 5/8 in., as at Kellogg, to a maximum of about 2 in. The electrodes must hang absolutely true to avoid short circuits and to ensure even distribution of current. Some sort of guide must be used, and the period of deposition must be shortened, when close spacing of electrodes is practiced.

The edges of the cathodes present sharp surfaces that tend to become points of higher current density than the rest of the surface. This effect is conducive to the formation of "trees." Anode sheets are usually made smaller than cathode sheets to reduce this effect. The use of strips on the vertical edges of the anodes helps to reduce the formation of "trees" and prevents undue warping of the anodes.

Bus Bars and Tank Bars.—Copper, either rolled or cast, is universally used for bus bars. Cast bars are usually cheaper than rolled, especially if odd shapes are required. The usual method of determining the size of bar required is to allow 1 sq. in. of cross-sectional area for each 1000 amp. With large bars, however, this does not allow enough radiating surface to avoid overheating. If 8000 to 12,000 amp. is to

[1] The lead-silver anode was originally worked out by U. C. Tainton, apparently largely from theory, and was a great factor in enabling him to produce four-9 and even five-9 zinc. The Tainton anode has about 40 per cent of its surface replaced by holes. For a description of the work on this anode, see Lead Alloys for Anodes in Electrolytic Production of Zinc of High Purity, by U. C. Tainton, A. G. Taylor, and H. P. Ehrlinger, *Trans. A.I.M.E.*, February meeting, 1929.—EDITOR.

be carried by the bar, the cross-sectional area allowed for each 1000 amp. should be at least 1.25 sq. in. Thus, cast-copper bus bars having a cross-sectional area of 10 sq. in. are recommended for a circuit carrying 8000 amp. The several lengths of bus bars are joined with machined lap joints bolted together. These joints must be inspected from time to time and the bolts tightened to ensure perfect contact; this is especially important during periods in which there have been large fluctuations in loads causing expansion or contraction.

Tank bars are used to connect the cell electrodes in parallel with each other and in series with the next cell in line. The greatest load, therefore, is at the center of

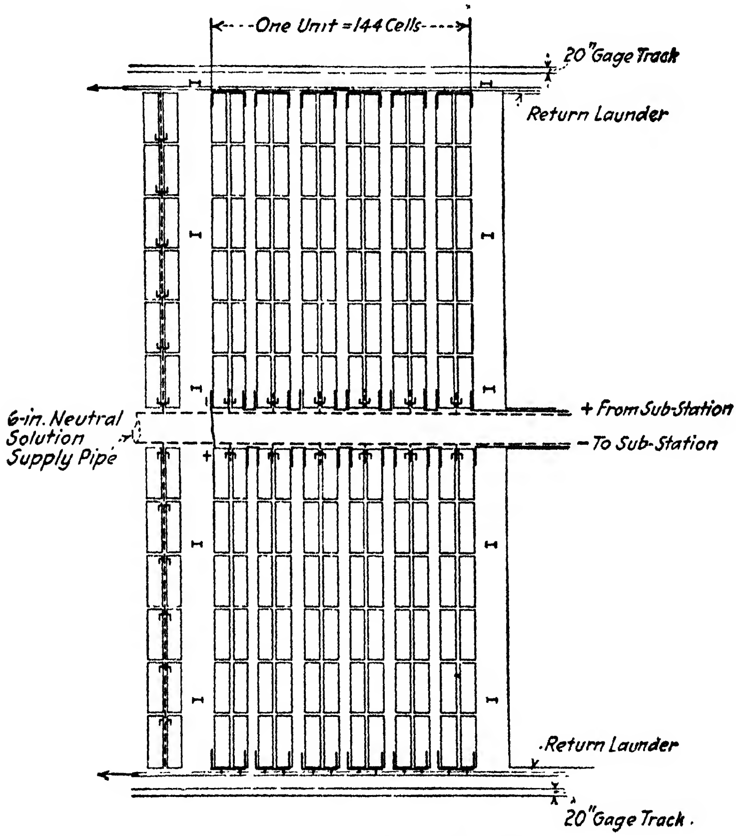

FIG. 9.—Tank layout, Great Falls.

the bar, and the smallest load is at either end. From the standpoint of first cost and working conditions, a bar larger in the center and tapering toward the end is the best. Then, at the point of connection to the main bus-bar line, the anode tank bar has the same area as the bar line, but, as the current is distributed to the individual anodes, the area decreases to a theoretical zero cross section at the end of the tank. The cathode bar starts at zero cross section and gradually increases in area as the load increases until it reaches the full area of the bar line and, passing to the next tank, becomes the anode bar and again gradually decreases to zero area. By using tapered bars and placing the bars on only one side of the tank, all bars in each group of tanks in solution series can be double bars. This system enables both the anode and the

cathode tank bars to be placed on the working side of the tank where they may be kept polished without leaning over the tank. The insulated ends of both the anode and cathode supports are in this case on the opposite side of the tank from the contact ends. The total amount of copper required on the tank with this system is only a little more than two-thirds of that required when using a common center bar, and about one-half that required if single bars are placed on each side of the tank.

Tank bars may be supported on the top edge of the tank, on the side of the tank, or by separate supports. When carried on the top edge of the tank, they are usually placed with the flat side resting on the supporting surface. When carried on the side of the tank, the normal practice is to place the bars on edge. In either case, the

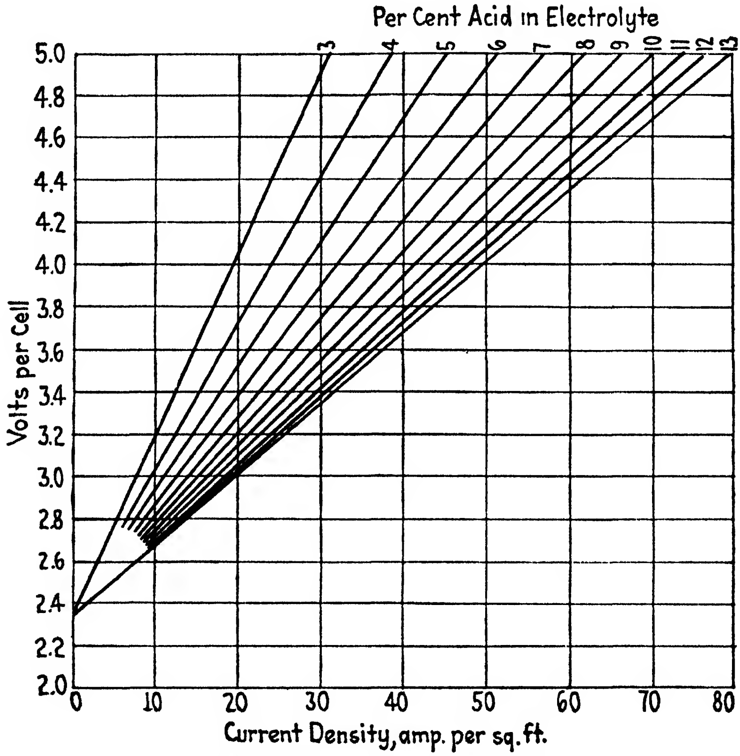

FIG. 10.—Cell resistances, 2-in. electrode spacing at 35°C.

outer bar is slightly higher than the inner so that contact can be made with the cathode or anode support bars without interference with each other. Separate support bars can be arranged in any manner to suit local ideas or conditions. The advantages of carrying the tank bars on the sides of the tanks are: a greater percentage of the electrode surfaces is rendered effective through reducing the space between the electrode supports and the solution level; contacts and tank-bar insulation are placed entirely outside the tank, simplifying the problem of keeping contacts clean and insulation dry; a smaller amount of acid mist or vapor comes in contact with the tank bar, reducing corrosion; a greater circulation of air around the bars is obtained, aiding cooling; and the copper sulphate formed by corrosion of the tank bars can be washed off without falling into the electrolyzing cell. The main disadvantage of the system is the necessity of supplying greater aisle space.

Insulation.—Tanks are insulated from their foundations by glass blocks or porcelain insulators between the tank supports and foundations. Wetting of these insulators by solution leaks can be prevented by covering them with sheet-lead caps. The electrode-support bars and tank bars are insulated from the tanks by wood strips and blocks impregnated with tar, oil, or other waterproofing material. Bus-bar lines are supported on glass or porcelain insulators or are suspended by some type of strain insulators from the tank-floor supports. Solution and water lines are insulated by the insertion of rubber-hose connections in the lines, and by supporting the lines on wood or tile blocks. All insulation must be of nonabsorbent materials to avoid wetting by condensation of water vapor from evaporation in the cells, and from the mist carried by gas from the cells.

Arrangement of Cells.—As many cells are placed in series, electrically, as the power equipment will permit. The maximum voltage limit of the direct-current

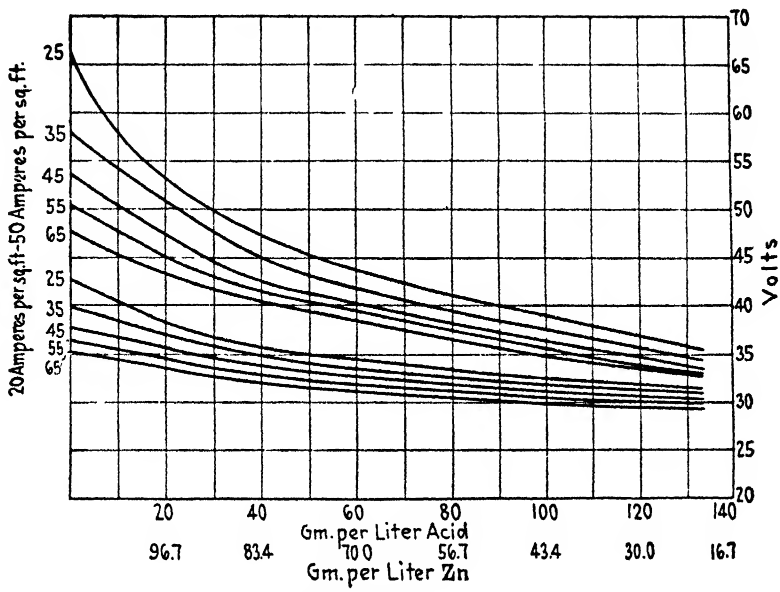

FIG. 11.—Electrolyte resistance, 4-in. anode spacing.

equipment divided by 3.75 is a safe figure to use in determining the number of cells to be connected to one power unit. The absolute maximum load should not be attempted as some leeway is desirable from an operating standpoint. Some of the earlier plants were designed for a maximum of 4 volts per cell, but this figure has been found to be too conservative.

As many cells may be placed in series or cascade, as regards solution flow, as is desired. Six to nine cells in solution series is the usual number. Working conditions and economy are the determining factors. The grouping at Great Falls and Risdon is in cascades of six cells. Twelve cells are placed side by side, as closely as safe insulation will permit, in a double row or cascade. This arrangement saves space as the working aisles are between each double row. Tank bars are placed on the sides of the tanks next to the aisles, leaving the inside tank edges for the insulated ends of electrode support bars. This arrangement is shown in Fig. 8. At Trail, the tanks are placed in a series of nine to a cascade. The two tanks side by side in each double cascade are constructed as a single unit with a common center wall.

By placing more cells in a cascade, less floor space and less copper are required; but the cathodes must be transported further for stripping, and more operating labor is necessary. It is customary, when tanks are to be cleaned, to cut a double cascade out of the electrical circuit at one time. Therefore, with the same number of cells per unit, the greater the number of tanks per cascade and the greater the proportion

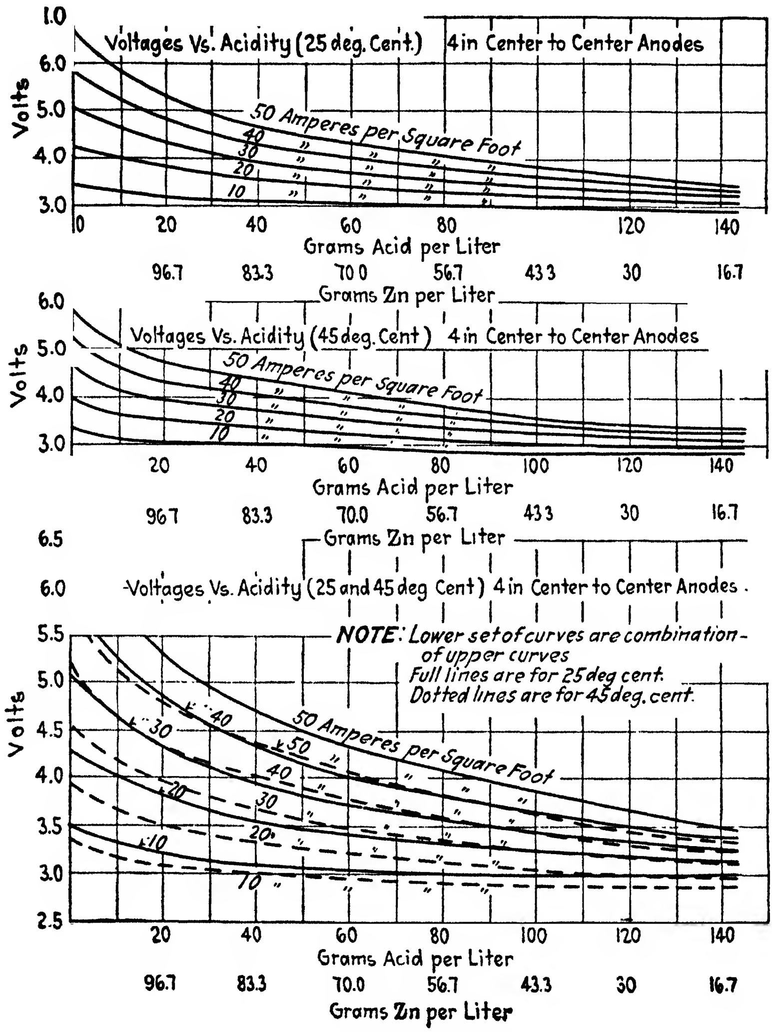

FIG. 12.—Electrolyte resistance.

of a unit cut out for cleaning. Any accidents, such as the breaking of a solution feed line over a tank or a leak in the roof of the building, which might wash impurities into a cell and contaminate the following cells in a cascade, are less serious if only a few cells are in series.

Solution System.—Solution to be fed to the electrolyzing cells is usually pumped into storage tanks placed at sufficient elevation to give a gravity flow from the storage

to the cells. Iron pipes may be used to conduct this solution to the cells as it is neutral in reaction and free from copper. Lead lines with flanged joints are preferable to iron, however, as some basic zinc sulphate and calcium sulphate are precipitated from the solution as cooling progresses, and build up in iron pipe more quickly than in lead. Also, there is always more or less danger of external corrosion of iron lines through occasional leaks of acid solution and by the condensation of acid mist from the cells. The feed lines are usually carried under the floor along the upper cells of the cascades, and a riser tapped in for each double cascade. A pipe line extending the full length of the cascade is connected to the riser, and each cell of the double cascade can be fed through branches equipped with valves to regulate the flow to each. Wood launders over the cells are used as header lines to carry the solution to the cells at the Magdeburg plant. The individual cells in this system are fed by means of rubber siphon hoses from the launder to the cells. The problem of regulating the flow in the launder to prevent spills and the extra space above the cells taken up by the launders prevent this system from being easily adaptable to the usual arrangement of electrolyzing cells.

At Great Falls, solution is fed into the head cell of each cascade at a rate that will maintain the acid strength in that cell at slightly less than the discharge from the last cell of the cascade. The first cell discharges into the head end of the second cell, the second into the third, and so on down the cascade. The last cell discharges into a launder that carries the spent electrolyte to storage tanks for the leaching plant. Neutral solution is fed into each cell but the last in sufficient quantity to maintain practically constant acidity throughout the cells, except the last, in a cascade. The last cell brings the acidity up to the desired strength or, from another viewpoint, depletes the zinc content to the desired point, thereby acting as a control cell. The acid content of each cell is determined at regular intervals and the feed to each cell so regulated as to give the desired acidity. By maintaining practically constant acidity in each cell, the voltage required is kept at a minimum. It is unnecessary to mix any acid with the neutral feed solution in order to keep the acidity of the upper cells up to the average. Each cell generates its own acid requirements and receives its own portion of feed, except that the lowest cell in each cascade usually receives only the discharge from the cells above it.

The rate of flow increases from the first to the last cell, the volume being cumulative; but no improvement in efficiency of the cells having the higher rate of flow has been noticed. No baffling arrangement is necessary to maintain an even distribution of solution in the cell as the gas evolution at the anode is sufficient to supply the necessary circulation. As the current density increases, the rate of zinc deposition increases, with an increased evolution of oxygen at the anode, and the gas evolved increases the rate of circulation proportionately to the requirement of fresh solution at the electrodes.

Cooling.—The electrolytic-zinc cell operates best at a temperature of between 35 to 45°C. A large proportion of the power delivered to the electrolytic-zinc cell is dissipated as heat, and the amount of heat dissipated increases with an increase in current density. Some heat is carried out by the spent electrolyte and some is radiated, but at the current density usually employed in practice, it is necessary to supply some additional cooling. This is usually done by passing water through coils placed in the cells. A current density of 30 amp. per sq. ft. or over requires at least 50 ft. of 1-in. cooling coil for each cell. The amount of cooling water passed through the coils depends on the temperature of the water and the efficiency of heat transfer in addition to the other cell conditions of current density, acidity, electrode spacing, etc. In any case the amount of cooling water needed is quite large and will vary from 6 to 8 gal. per min. for each ton of zinc produced per 24 hr.

Cooling coils are commonly made of lead, as most other materials that have been tried are not satisfactory either in their ease of construction, resistance to corrosion, physical strength, or ability to transfer heat efficiently. Two to four coils are used in the ends of each cell. Lead pipe of approximately 1 in. in diameter is usually used. The cooling water is not usually passed through a single coil, but two or three coils are placed in series in order to obtain the greatest possible amount of cooling from the water. The cooling water supply is carried in mains, which may be of iron pipe, but the connections between the main and the lead coils are made with short lengths of rubber hose which act as insulators. The actual amount of fresh water necessary for cooling purposes can be reduced by using a closed system and by passing the heated water through spray chambers. In this case the only additional water necessary is that needed to replace the amount lost by evaporation.

Stripping Equipment.—All methods of stripping the zinc deposit from the cathode —from removing one plate at a time to removing all the plates in a cell at one time— have been tried. The removal of one plate at a time is too slow and expensive, and removing a full tank at a time means a large loss of production and danger in "shorting" the tank before removing the plates. In addition to this, when all the plates are removed at once, some power-driven lifting device is necessary. If many plates are removed simultaneously, the current density on the remaining plates is greatly increased. If only one-third of the total plates are removed from the cell, the remaining plates are able to carry the current for the length of time necessary to strip the zinc.

At Great Falls the cathode sheets are lifted with hand-operated chain blocks running on I beams placed over the center line of each cascade. Nine sheets are lifted at a time, using a special rack. This lifting rack has sawtooth sides, and the teeth in the sides are spaced to correspond with the cathode spacing. The rack in use is placed on the cathode bars, and, as the load is raised, the spaces between the teeth on the rack engage lugs riveted to the cathode support bars. At the lower end of each cascade is placed a stand having nine pieces of 3-in. channel iron, the centers of which are spaced the same as the cathode spacing. A lengthwise slot is cut in the center of each channel iron into which a cathode sheet can be slipped and held upright. One end of each channel iron is bolted loosely to a supporting stand in such a manner that it can be moved in a horizontal plane. The load of cathodes is brought to this stand and the cathodes slipped into the slots in the channel irons. The load is lowered until the cathode support bars rest on the channel irons and the lifting rack is disengaged from the lugs. The outside sheet of zinc is removed from the first cathode; then the channel supporting that cathode is swung to one side, and the inside sheet of zinc removed from the same cathode. The adjacent side of the second cathode is exposed when the first is swung over. This second cathode is stripped on one side and then swung over and stripped on the other side. After all nine cathodes have been stripped in this manner, they are swung back into their original position and lifted with the lifting rack. The cathodes are returned to the cell from which they came, being held correctly spaced in the lifting rack.

A heavy knife is used for stripping the zinc deposit from the cathode. The deposit is struck a sharp blow at one corner with the edge of the knife to loosen it slightly from the surface of the aluminum cathode. The point of the knife is slipped under the loosened corner and twisted to break loose the deposit. If the zinc deposit adheres tightly to the cathode, a wooden mallet is sometimes used to aid the knife in breaking it loose. The zinc sheets, as stripped, are placed on small narrow-gauge cars. These cars are used to transport the cathodes to the melting furnaces.

Operation of the Cells.—Starting with clean cells, new electrodes, and neutral solution, the resistance of the zinc cells is so great that little current flows for several hours after power is put on the circuit. The addition of some pure acid, such as spent

electrolyte, immediately increases the flow of current by reducing the resistance. If no acid is available, the flow of current is permitted to increase as rapidly as decreased resistance, through the formation of acid, will permit. Some resistance may be removed by "shorting" one or two groups of cells in the unit until some current is flowing. It is customary, when starting up a unit from which the acid solution has been drained, to add some spent electrolyte to it from other units already operating. This shortens materially the time necessary to get the unit into normal production.

Starting with neutral solution, the zinc deposited in the first 24 or 48 hr. will be rather spongy. This condition is due to the low acidity of the cells; and the zinc deposit should be stripped as soon as it is thick enough to break loose from the aluminum blank. As soon as the deposited zinc begins to show a bright surface, the period of deposition can be increased to the normal length of time. When the acid strength gets up to 2 or 3 per cent, a small flow of neutral solution is started in the upper cells of the cascade and is gradually extended to the lower cells as the acidity increases, so that the solution in none of the cells becomes too low in zinc content. Acid strength is usually not allowed to get above about two-thirds normal until the full period of deposition is started. Full current density is generally not permitted until the deposited zinc has been stripped once or twice.

The amount of zinc stripped per man-day varies with the period of deposition and with the location of the plant. At Great Falls, using a 24-hr. period of deposition, each man cares for and strips the zinc from 12 cells. This is approximately 4 tons of zinc. At Trail, each man strips between 5 and 6 tons of zinc per day; and at Risdon, using a 72-hr. deposition period, each man strips between 8 and 9 tons of zinc per day.

Control of acidity is very important in the operation of the cells. Frequent tests of the acidity are necessary. These tests can be made by titration with standard sodium carbonate solution, by use of a hydrometer, or with an electrical-measuring device.

The electrolyzing cells must be periodically cleaned for several reasons. Many ores contain soluble manganese, and some manganese is used to oxidize iron in the neutral leach and is dissolved in the solution. Part of the manganese in the electrolyte is precipitated at the anode as manganese dioxide. Some of the precipitated MnO_2 adheres to the anode as a flaky covering, and the remainder settles to the bottom of the cell as a sludge. When the manganese dioxide in the cell exceeds a certain amount, depending upon the operating conditions of the cell, it must be removed. The insulation on top of the cells gradually becomes impregnated with solution and must be periodically renewed. The tank bars become covered with copper and zinc sulphates and must be cleaned at regular intervals. A double cascade of cells is usually cleaned at one time. The double cascade is cut out of the electrical circuit, the electrodes are removed, the solution is pumped out, and the manganese sludge is removed. The insulation is renewed, the tank bars are cleaned and replaced, the electrodes are cleaned, straightened, and replaced, and the cells are refilled with acid and solution. The double cascade is then put back into the electrical circuit. If a spare cascade is available, the cleaning cycle can be carried out in a systematic manner without loss of zinc production during the shutdown period.

Care of Workmen.—Rubber shoes should be supplied to insulate the men working in the electrolyzing room. Besides affording the worker protection from becoming "grounded" between the main circuit and the floor, the shoes also save him from a considerable amount of annoyance from stray currents which, although usually harmless, are always likely to be present. The acid solutions encountered in the electrolyzing room are very hard on garments made of cotton or mixed wool and cotton. The workmen in the cell room are usually given a clothes allowance or furnished clothing made of pure unwashed wool. Great care must be given the hands

of men coming in contact with acid zinc sulphate solution, otherwise cracks and sores, especially around the fingernails, will result. Rubber, or rubberized canvas, gloves are often used by the workmen. The spray rising from the electrolyzing cells is largely oxygen, but each bubble of gas is surrounded by a film of acid solution which is very corrosive to the nasal passages. Several thicknesses of sterilized cotton gauze placed over the nose and mouth will effectively filter out this spray. Each man should be furnished with fresh gauze every working day. No occupational disease has resulted from this work, nor has any extra trouble been experienced in obtaining men for this work.

A frothing-agent is added to the cells at Kellogg to prevent the formation of spray. This agent is very effective when used in a solution of small volume and high zinc content, but it is not satisfactory in a low-acid system.

Voltage.—The theoretical decomposition voltage of zinc sulphate solution is approximately 2.35 volts, but the best operating conditions require 3.25 to 3.50 volts, depending on current density, temperature, acidity, spacing of electrodes, and the period of deposition. With constant acidity, temperature, etc., the voltage increases rapidly with increased current density, as shown by Fig. 12. Resistance of solution is decreased by increasing acidity; this effect is quite marked up to 10 per cent H_2SO_4, but proceeds more slowly above 10 per cent H_2SO_4. With 30 amp. per sq. ft. current density, and with an acidity of 5 per cent H_2SO_4, the voltage required is about 4.0 volts per cell at a temperature of 35°C. An increase in the acidity to 12 per cent, with all other conditions the same as before, reduces the voltage to 3.4 volts. If the temperature and the acidity are both increased, the decrease in voltage is even greater. High temperatures are not desirable in the electrolyzing cells from the standpoint of the increased effect of impurities on ampere efficiency. A high temperature is, however, advantageous in reducing the power cost of electrolyzing a solution low enough in impurities so that a good ampere efficiency can be obtained. In other words, it pays to supply the cells with a solution of sufficient purity so that a reasonably high temperature and acidity can be maintained. At Great Falls, a temperature of over 50°C. has been maintained for several weeks at a time with a current density of 30 amp per sq. ft. During these periods an ampere efficiency of 90 per cent was obtained when a deposition interval of 24 hr. was used.

The spacing between anodes and cathodes affects the voltage required for electrolysis, but cannot be safely reduced much below 2 in. without the use of special equipment to hold the electrodes in place. Electrodes have a tendency to warp during continued use with serious results if close spacing is used. Also they may not hang absolutely true, because of unevenness in the surface of the contacts between the support and tank bars, unless special guides are used.

Ampere Efficiency.—The ampere efficiency of electrolysis is calculated by dividing the actual yield of metal by the amount that theoretically should have been obtained from the current used. This result multiplied by 100 gives the percentage ampere efficiency of the process. One ampere-hour should theoretically deposit 1.219 g. of zinc from a solution. In actual practice, however, it is very seldom that an ampere efficiency of over 95 per cent of the theoretical is ever obtained for any length of time. At a current density of 30 to 40 amp. per sq. ft., an ampere efficiency of 92 to 94 per cent is considered good work. The factors that influence ampere efficiency in the operation of the zinc cell are the purity of the solution, the temperature of the cell, the effectiveness of addition agents, the period of deposition, and the ratio of zinc to acid in the solution.

Some harmful impurities can be present in much larger amounts than others without seriously affecting ampere efficiency. A great deal of work has been done to determine the effect of single impurities and to set safe limits for the amounts that

can be present in the solution without loss in current efficiency. The effect of any impurity, and the amount that can be tolerated, is strongly influenced by the other conditions that may be present during electrolysis. For this reason, the results of different experimenters do not always agree, but some fairly accurate averages have been obtained for the common impurities. The combined effect of two or more impurities, each present in an amount less than the safe limit for that impurity, is a much more involved problem than that concerned with the effect of single impurities. The

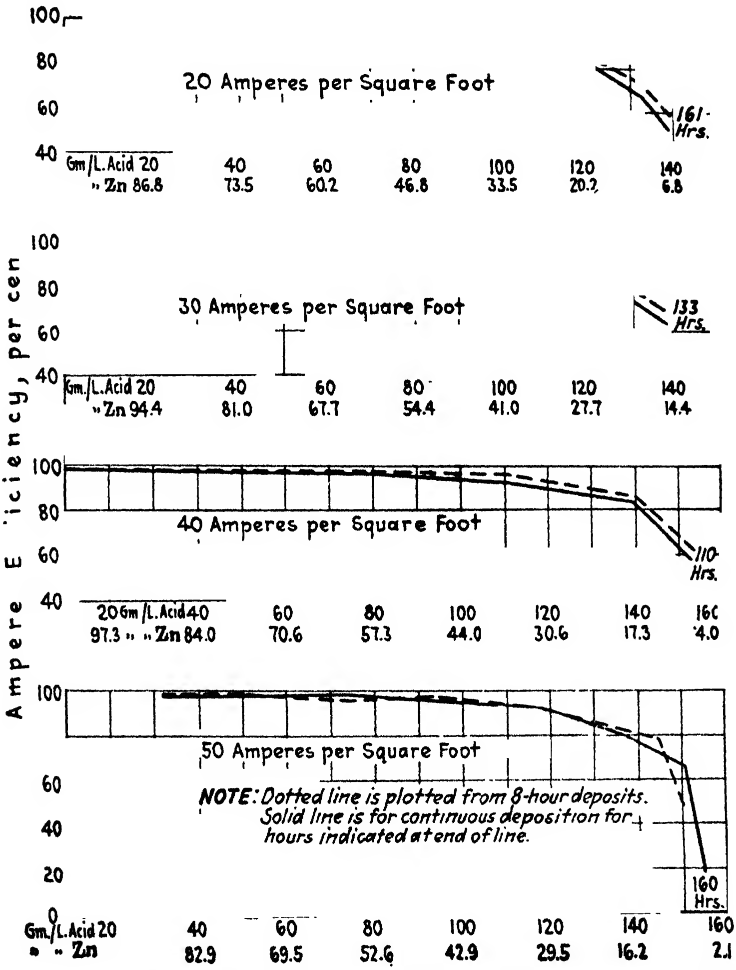

FIG. 13.—Effect of time of deposition and ratio of zinc to acid on ampere efficiency.

effects of some impurities, even in minute amounts, are greatly aggravated by the presence of certain other impurities. The enormous number of impurity combinations possible, when coupled with the many variations of operating conditions encountered in the process, prevents any easy solution of the problem. It may be that in the future some general rule relating to the problem can be evolved; but at the present time the information pertaining to the effect of impurity combinations deals only with certain specific conditions occurring in individual plants, and not generally applicable to the process.

The temperature at which the zinc cell operates is an important factor affecting ampere efficiency. The detrimental action of impurities is increased greatly, and the hydrogen overvoltage on zinc is lowered, by a rise in temperature. The optimum temperature for a zinc cell operating between 30 to 40 amp. per sq. ft. is usually to be found between 35 to 45°C. The operating costs required to cool the solution below 35°C. are usually more than the saving in ampere efficiency, while above 45°C. a good ampere efficiency can be obtained only when the solution to be electrolyzed is exceptionally free from impurities.

The period of deposition affects ampere efficiency; as the period of deposition increases, the effect of any impurity becomes more pronounced. With absolutely pure solution, high ampere efficiency can be obtained with 48-, 72-, 96-hr. or even longer periods of deposition. In plant operation it is frequently found advisable to decrease the period to 24 hr. or less. At Kellogg, using high current density, the period is 8 to 12 hr. Risdon, on the other hand, commonly operates with a deposition period of 72 hr., without any great loss in current efficiency. Most other plants use either a 24- or 48-hr. period. The length of time that zinc can be efficiently deposited is influenced by other cell conditions such as temperature, current density, acidity, and the effectiveness of addition agents. The most efficient period for each individual plant must be determined by balancing the extra labor cost for more frequent stripping against the power saved through improvements in ampere efficiency.

The ratio of zinc to acid in the solution necessary to maintain maximum ampere efficiency varies with all the other cell conditions. The usual practice is to deposit from solution about two-thirds of the zinc content of the neutral solution, and to return the other one-third to the leaching plant. If the amount deposited greatly exceeds this ratio, some loss in ampere efficiency will result. A cell in which the solution becomes greatly depleted in zinc has a tendency to evolve hydrogen. This condition can also be reached if the circulation of solution within the cell is not sufficient continually to supply all parts of the cell with an adequate amount of zinc ions. An excessive amount of circulation, however, is not desirable as it aids the rate of corrosion by increasing the amount of acid brought into contact with the deposited zinc. Here, as in the other operating conditions, the best rate of circulation must be determined experimentally.

Addition agents such as glue, goulac, and metal salts are often used to aid ampere efficiency and to improve the physical character of the zinc deposit. Glue is the most commonly used addition agent, but its use is becoming less as improved methods of purifying the solution are developed. It is not good practice to rely on the use of addition agents if it is possible properly to purify the solution to be electrolyzed. The addition of one impurity in order to inhibit the action of another is more in the nature of an evasion than a real solution to the problem. On the other hand, electrolytic-zinc plants must be operated at a profit, and any method to obtain the desired results should be employed until a better has been developed. Nearly all plants use some sort of addition agent at the present time. The presence of an unusual amount of cobalt in the electrolyte at Risdon, Tasmania, has made good ampere efficiency economically impossible without the use of addition agents. A combination of glue, beta-naphthol, and antimony is added to the electrolyte at Risdon, and ampere efficiencies of 92 to 94 per cent are obtained over a 72-hr. deposition period.

Another important factor that must be taken into consideration is the influence of workmen on ampere efficiency. Good workmen, conscientious in their care of the electrolyzing cells for which they are responsible, can consistently get higher efficiencies on their cells than can workmen who are somewhat careless. In some plants a bonus is paid to the workmen who, by careful attention to detail, are responsible for the production of more than a certain specified amount of metal.

Effect of Impurities.—The effects of single impurities on zinc electrolysis may be determined experimentally if certain necessary precautions are taken. In order to be certain of the results obtained, it is necessary to start with an absolutely pure solution of zinc sulphate; otherwise the result will be a combined effect of the added impurity along with those already present. A zinc sulphate solution prepared from the so-called c. p. zinc salts is not satisfactory for this work without further purification. The difficulty in applying any set of data on the effect of single impurities to actual plant operation is that a plant solution containing only one impurity is never obtained. Also, the experimental data are obtained with certain specified cell conditions which if varied cause a change in the effect of the impurity. These specified cell conditions are difficult to maintain with commercial operations on a large scale. The experimental data obtained have, however, been of great value as a basis from which to guide purification practice and as an aid to the recognition of the most injurious impurities. The experimental data have also enabled the operators to determine the presence of some impurities from the appearance of the zinc deposit without waiting for a complete analysis of solution.

The impurities encountered in the electrolysis of zinc may be classified, according to their general effects on the cell, as cathodic impurities, anodic impurities, and beneficial impurities.

Cathodic impurities have the greatest effects upon the efficiency of zinc deposition, and their elimination or control is one of the major problems in electrolysis. When a metallic salt is present in an acid solution and an electric current is passed through the solution, either the metal can be deposited or hydrogen can be evolved. When the decomposition voltage of the metallic salt present is above that of water, hydrogen is usually evolved. This is not true in the case of zinc, lead, or cadmium, however, owing to the high hydrogen overvoltage on these metals. In the case of zinc, the decomposition voltage of zinc sulphate is 2.35, and that of sulphuric acid on a zinc surface is 2.4. Therefore, zinc will be deposited at the cathode in preference to hydrogen unless, owing to the presence of certain impurities, the hydrogen overvoltage on zinc is lowered below the decomposition voltage of sulphuric acid. If any impurity, which lowers the hydrogen overvoltage on zinc to the point where hydrogen can be evolved, comes into contact with a zinc surface during electrolysis, hydrogen will be evolved on the surface of the impurity and zinc will be dissolved. The cathodic impurities can be further classified according to their effects on electrolysis. The first group includes those metals whose sulphates decompose at a higher voltage than zinc sulphate. The common elements of this group are aluminum, sodium, potassium, magnesium, and manganese. They have no effect on electrolysis so far as reactions at the cathode are concerned. The second group includes those metals whose hydrogen overvoltage is high enough not to cause the re-solution of zinc, but whose decomposition voltage is less than that of zinc. The common elements of this group are lead and cadmium. These have no detrimental effect on the efficiency of zinc decomposition; in some cases they may even be beneficial. They do, however, deposit with the zinc and cause an impure product. The third group includes those metals whose hydrogen overvoltage is below that of zinc but whose decomposition voltage is above that of sulphuric acid. The common elements of this group are iron, nickel, and cobalt. These metals are injurious to electrolysis, but do not ordinarily contaminate the deposited zinc. They are soluble in acid and consume power by being alternately deposited on the zinc surface and redissolved in the acid electrolyte. They are particularly detrimental to electrolysis when present in combination with certain other impurities. The fourth group includes those metals of which the sulphate decomposition voltage is below that of sulphuric acid and the hydrogen overvoltage is low enough to cause re-solution of zinc. Copper, arsenic, germanium, and antimony

belong to this group. They are deposited with the zinc and form points of low hydrogen overvoltage where hydrogen is evolved at the expense of the zinc. This group is the most injurious of all impurities. The commonly met cathodic impurities can all be classified in these four groups when present as single impurities; but combinations of two or more impurities, especially if from different groups, cannot be so easily classified.

The anodic impurities include all the anions except those of sulphuric acid. The common ions of this group are manganate, permanganate, chloride, chlorate, perchlorate, and fluoride. Their effect on electrolysis is not so violent as that of the metallic impurities, but they very often have a distinct bearing on the amount of corrosion occurring in the zinc cell. Some of them increase corrosion, and some aid in preventing it. Those anions which increase corrosion of the lead anodes cause an increase in the amount of lead deposited with the zinc. Those ions which increase corrosion of the aluminum cathode cause the deposited zinc to cling tightly to the sheet. This is commonly known as "sticking," and can become so intense that the zinc deposit can be removed only by dissolving in acid.

The beneficial impurities include all those used as addition agents. While these impurities may not be beneficial when used in an absolutely pure zinc sulphate solution, they are often used to prevent the more detrimental effects of certain other impurities. Some addition agents are beneficial in causing a smoother, harder deposit of zinc. Glue is an example of an impurity of this type. Manganese in the electrolyte accumulates on the anode in the form of manganese dioxide and tends to protect the anode from corrosion.

J. T. Ellsworth, at Park City, Utah, obtained data on the effects of single impurities that are as accurate as any that have yet been published. The results of his work were published in Volume 42 of the *Transactions of the American Electrochemical Society*. Ellsworth prepared a solution of zinc sulphate by burning zinc of high purity to form zinc oxide and dissolving this in pure sulphuric acid. This solution was then purified by agitation with zinc dust to remove the last traces of copper and cadmium. Definite quantities of each impurity tested were added to separate portions of the solution, and each was electrolyzed under a standard set of conditions.

Antimony is one of the most injurious impurities encountered in electrolytic-zinc operations. Its effect is noticeable at high temperature and high acidity if present in only minute amounts. One part per million is apparent even at the normal cell conditions of low temperature and acidity. The zinc becomes spongy and dark in color; sprouts, small at the surface of the zinc and large at the end, form in large numbers; and ampere efficiency is much lower. The longer the period of deposition, the greater will be the effect of the impurity. The remedies applied are a more thorough purification in the neutral leach, a shortening of the period of deposition, and a lower cell temperature. At Risdon, however, a small amount of antimony has been found beneficial when there is an unusual amount of cobalt in the electrolyte.

Arsenic, when alone, is much less injurious than antimony. The presence of arsenic in solution, however, is a pretty sure indication that some antimony is also present. Arsenic and antimony are both removed by the same methods of purification, but arsenic is eliminated more easily than antimony. Therefore, antimony may be present in small amounts without any arsenic, but arsenic is rarely present without antimony unless an ore free of antimony is being treated. The first indications of the presence of arsenic in the zinc cell are pronounced corrugation of the surface of the zinc deposit and the absence of the usual luster on the deposit. This is soon followed by sprouting and by a serious loss in ampere efficiency. There is really no excuse for the presence of arsenic in the electrolyte if efficient methods of control are used in the neutral leach.

Cobalt will cause re-solution when present in amounts as low as 10 mg. per l. unless special treatment is used. At Risdon, an addition agent consisting of glue, beta-

naphthol, and antimony is added to the solution in order to prevent the loss of current efficiency in the presence of larger amounts of cobalt than are usually encountered. Small amounts of cobalt can ordinarily be minimized in their effects by the use of glue alone. Cobalt is the most serious impurity commonly encountered in the process. While its detrimental effects are not so violent as a like amount of antimony, its removal is much more difficult. The pernicious influence of cobalt is much more marked when accompanied by germanium than when present alone. Small amounts of cobalt are eliminated by the regular methods of purification, but when present in large amounts it must be removed by special purification methods. Although cobalt lowers current efficiency, its presence in the electrolyte has a beneficial influence in lowering the amount of lead in the deposited zinc.

Germanium when present in amounts as low as 1 part in 10 million may produce adverse effects on the zinc deposit. Although very injurious when present alone, it is especially detrimental when accompanied by certain other impurities. For example, germanium in amounts too low to be detected by ordinary analytical methods will show a decided effect on electrolysis when cobalt is also present in the solution. Germanium, when present in small amounts, is usually eliminated by the iron hydroxide purification in the neutral leach. Some germanium is also removed by the regular zinc-dust purification if sufficient copper and cadmium are present. When present in any appreciable amounts, however, adequate removal of germanium requires special methods of purification.

Nickel has somewhat the same effect as cobalt. When alone, a concentration of 0.0001 g. per l. has no particular effect on ampere efficiency. Any amount above 0.0005 g. per l., however, is very injurious. Nickel causes the re-solution of the zinc deposit, and may also be found in the deposited metal. Nickel is not commonly found in appreciable amounts in zinc-plant solutions. When present, it can be removed with zinc dust if the solution is heated to a high temperature during the purification.

Copper may be present up to about 10 mg. per l. without much harm to ampere efficiency, and with a low acidity, the amount of copper may go even higher without serious results. If the usual methods of removing cadmium from solution are carried out far enough to produce high-grade zinc, there should never be any great danger of copper entering the zinc cell from this source. If uncoated copper support bars and tank bars are used, the corrosion of copper by the acid mist and by drippings must be considered as a source of copper in the cell. A great deal of care should be taken not to wash or knock the copper sulphate formed in this manner into the cells. The amount of copper so introduced is normally too small to affect the zinc deposit materially; but occasional breaks in water or solution lines, or leaks in the cell-room roof, may wash enough copper into a group of cells to cause violent re-solution in the cells affected. The quickest remedy for a condition of this sort is to run fresh solution into these cells in order to lower the acidity and to remove the fouled solution as soon as possible. The cathodes should also be removed and the deposited zinc stripped immediately to prevent it from going back into solution.

Cadmium, when present in amounts not to exceed 0.5 g. per l., does not lower ampere efficiency or injure the physical condition of the zinc deposit. In fact cadmium in small amounts has been claimed to increase ampere efficiency. Cadmium must, however, be removed from the solution previous to electrolysis if grade A zinc is to be produced. The elimination of cadmium is usually accomplished by the regular methods of purification.

Lead, like cadmium, is plated out with zinc during electrolysis. Lead sulphate is practically insoluble in zinc sulphate solution, and only very minute amounts are ever found in the solution fed to the cells. The greatest source of lead in the zinc cell is from corrosion of the lead anodes or the lead tank lining of the cell. Any factor, then,

that will reduce the corrosion of lead in the cell will lower the amount of lead in the deposited zinc. A further discussion of lead in cathode zinc will be found later under the heading Purity of Zinc Metal.

Iron in amounts up to 0.02 to 0.04 g. per l. has no noticeable effects on ampere efficiency. Above that amount, iron begins to cause trouble. Ferrous iron is oxidized at the anode to ferric iron, which in turn is reduced to ferrous iron at the cathode. This reaction takes power and in this way affects the ampere efficiency. Large amounts of iron, especially when other impurities are present, may become detrimental to the character and grade of the zinc deposit. The presence of iron in the electrolyte is usually an indication that the iron was incompletely precipitated in the neutral leach and serves as a warning that the impurities usually removed with iron may also be present.

Manganese is usually classed as a harmless impurity. It has no great influence on ampere efficiency unless present in amounts above 3 g. per l. Large amounts of manganese cause the zinc to form a rough spongy deposit with many beads and sprouts. Manganese is deposited at the anode during electrolysis. The reaction is partly an electrical deposition and partly a chemical precipitation. Manganese sulphate is partially oxidized at the anode to permanganic acid, which in turn slowly reacts with more manganese sulphate to form hydrated MnO_2. This reaction is practically irreversible, and the precipitated manganese dioxide remains in the cell. Part of the MnO_2 adheres to the anode, and part falls to the bottom of the cell as a sludge. The amount that adheres to the anode seems to be dependent on the temperature and acidity of the electrolyte. The presence of certain other impurities such as iron or cobalt also influences the deposition of MnO_2 on the anode. Current density also seems to have some effect in this direction. Low acidity, low temperature, and low current density cause heavy anode coatings. If the amount of precipitated MnO_2 is so great that particles are occluded with the zinc deposit, these particles, being saturated with electrolyte, become individual cells. This "local action" is detrimental because large holes are formed in the zinc deposit.

Chlorine in amounts up to about 100 mg. per l. does not materially affect ampere efficiency. It does, however, increase the corrosion of lead anodes. Chlorides are easily oxidized at the anode to perchloric acid. Trail reports that the amount of perchloric acid formed is dependent on the oxidation potential of the anode. New anodes, for this reason, produce more than old anodes. Excessive amounts of chlorine may also have an effect on the cathode and cause the zinc deposit to adhere tightly. If the concentrate treated carries silver, the chlorine content of the electrolyte will usually be insufficient to cause trouble.

Fluorine has only recently been recognized as the chief cause of the zinc deposit "sticking" to the cathode. Any impurity or condition that causes corrosion of the aluminum cathode also causes sticking. The usual method of counteracting sticking is by conditioning the cathode to prevent corrosion. Various waxes, gums, and liquids have been used to produce a protective coating. The method used at Trail is to form a coating of aluminum sulphate on the cathode by a short "soaking" period in spent electrolyte. Fluorine is normally eliminated by the roasting process. There is no known commercial method of effectively removing fluorine from zinc sulphate solutions.

Nitrates, when present in the electrolyte, have much the same effect on the anodes as chlorides. Corrosion of lead is increased and the amount of lead deposited with zinc is larger when nitrates are present.

Sodium, potassium, magnesium, aluminum, calcium, etc., when present in the normal amounts, usually have no particular effect on ampere efficiency or on the physical character of the zinc deposit. Some of these elements are cumulative, however, and

if they build up to large amounts may become detrimental. At the Norway plant, for example, the concentrate contains so much magnesium that solution must be discarded at intervals in order to keep the magnesium content within satisfactory limits.

Current Density.—Current density is the strength of the electrical current used per unit of cross sectional area of the electrolyte. In the electrolytic-zinc industry, it is commonly expressed as amperes per square foot at the cathode. A wide range of current density may be used if all other operating conditions are properly adjusted. After a careful investigation of all the factors entering into the problem, all the large-scale producers have decided that a current-density range of 30 to 40 amp. per sq. ft. of cathode surface is the most economical and satisfactory density for their particular applications. Going much above 30 amp. per sq. ft. requires special provision for the cooling of solution and higher acidity to keep down abnormal power consumption. This higher acidity, in turn, requires a higher zinc content in the cell feed and is reflected in complications in the leaching system. If a current density much below 30 amp. per sq. ft. is used, the first cost of plant is high and the zinc deposited is not so firm as when deposited with higher densities. Local conditions determine the most economical current density for any particular installation.

An increase in current density is always attended by an increase in the power input to the cells because of the higher voltage required. The amount of voltage increase necessary will not be so great if the resistance in the cell is reduced by the use of a higher acidity and a closer spacing between the electrodes. When acidities above 12 to 13 per cent are to be maintained, the zinc content of the electrolyte must be higher than the saturation point of zinc sulphate at ordinary temperatures. Higher temperatures than usual must then be maintained in both the leaching and electrolyzing sections of the plant. High temperatures are beneficial in the purification and filtration steps of the leaching plant, but are often harmful in the electrolyzing cells. Settlement in the thickeners is hindered by an increase in density of the solution. Washing the residue after filtration is made more difficult by an increase in the zinc content of the solution, and the probable loss of water-soluble zinc is greater. If the resistance of the solution is reduced by closer spacing of the electrodes, the number of short circuits in the cell is likely to be increased. This condition adds to the cost of inspection and stripping. The effects of increasing current density under varying cell conditions are shown by the charts in Figs. 10 to 13. If the current density is increased much beyond the usual low-density practice, it might as well be raised to 100 amp. per sq. ft. or higher. The usual cooling equipment of a low-density cell room is not capable of sufficiently cooling the solution when high density is used. Also, if a current density higher than normal is used, special heating arrangements must be made in the leaching plant in order to prevent zinc sulphate crytallizing out of the supersaturated solution necessary to maintain the high acidity required.

Period of Deposition.—The period of deposition varies from the 8-hr. interval at Kellogg to the 72-hr. interval at Risdon. Shortening the period of deposition nearly always results in some increase in ampere efficiency, if all other conditions remain the same. When some harmful impurity is present, or if the temperature of the electrolyte is higher than normal, the effect of a variation in the deposition period is more pronounced than if the electrolyte is cool and of high purity. As the period of deposition is lengthened, the deposit gradually becomes rougher on the surface and tends to spring away from the surface of the aluminum sheet. The deposition period to be used is determined by balancing the benefits of increased ampere efficiency against the increased amount of labor required for more frequent stripping.

Purity of Cathode Zinc.—The purity of the zinc produced can be controlled partly by varying the cell conditions and partly by the amount of purification carried out

in the leaching plant. Purity of solution is the main factor influencing the purity of the metal. The impurity metals that deposit with zinc must be eliminated or controlled. The three impurities causing the most concern are cadmium, lead, and copper. The cadmium content of the zinc deposit is altogether dependent on the efficiency of the purification process. The lead content of cathode zinc is dependent both on the purity of solution and on cell conditions. The amount of copper in cathode zinc is almost entirely dependent on the amount of copper introduced into the cells by operating conditions.

The presence of lead in the deposited zinc is due mainly to corrosion of the lead anode. Normal electrolyte, when electrolyzed with platinum anodes, produces a deposit containing approximately 0.0002 per cent lead from soluble lead salts in the solution. The same solution when electrolyzed in a cell using lead anodes gives a much higher lead in the deposited zinc. The lead content of the deposited zinc varies with the operating conditions in the cell and increases with the age of the anode. If the lead anode is enclosed in a diaphragm, the amount of lead in the cathode zinc is greatly lowered. Any impurity, either in the solution or alloyed with the lead, that decreases the corrosion of the lead anode also decreases the amount of lead in the deposited zinc.

An ordinary lead anode consists of crystals of pure lead in a matrix of impure lead. This impure matrix is usually more soluble under the conditions of electrolysis than pure lead. As long as the crystals of lead are embedded in the anode, with a relatively small part of their surface exposed to the intense oxidizing conditions present at the anode, little lead peroxide is formed. When these crystals are set free, however, by solution of the matrix, they present a large surface to oxidation. Lead peroxide may either go into solution as lead persulphate and be deposited electrically, or it may be carried over to the cathode in the colloidal state and be occluded with the zinc deposit. When the anode is new, it takes some time before the matrix surrounding the crystals of lead is dissolved. During this period only a relatively small surface is presented for oxidation and the cathode zinc contains but little lead. If the anodes are replaced frequently, the quality of the zinc produced is improved. Any metal which, when alloyed with lead, tends to increase the resistance of the matrix to corrosion will lengthen the period during which the use of new anodes will produce a low-lead content in the cathode zinc. All the binary alloys of lead with the common metals have been investigated. A great many alloys containing two or more metals in addition to lead have also been tried.

The precipitation of manganese as a scale on the anode is often regarded as an aid in lowering the lead in cathode zinc. The formation of some scale is probably beneficial as a protecton against the action of certain anodic impurities. An excessive amount of manganese scale, however, tends to break away from the anode. This condition may become detrimental by mechanically carrying particles of lead peroxide to the cathode. The precipitation of manganese dioxide in the electrolyzing cell causes the eventual accumulation of a large amount of sludge in the bottom of the cell. Periodically the cells must be drained and this sludge removed. A frequent periodic cleaning aids in the production of zinc with a low lead content.

Any means of preventing lead dioxide from coming into contact with the cathode helps to lower the lead in cathode zinc. The use of a diaphragm surrounding the anode would be very effective in this respect, but no satisfactory form of diaphragm cell has yet been developed. The greatest detriment to the use of a diaphragm is the greatly increased corrosion of the anode caused by insufficient circulation in the cell. As soon as the diaphragm becomes partly "blinded" to free passage of the electrolyte, disintegration of the anode is enormously increased. An abnormal voltage drop between the anode and cathode accompanies this condition. Another, although

less serious, factor against the use of diaphragms in the zinc cell is the lack of a cheap satisfactory material.

The addition of any impurity to the electrolyte which will lower the oxidation potential at the anode is beneficial in the prevention of corrosion of the anode and aids in the production of low-lead zinc.

Miscellaneous Tank-room Notes.—Rotating-disk cathodes have been tried in place of stationary cathodes, with the hope of producing a heavier and smoother deposit. Their use has never been found to be satisfactory. Only about one-third of the rotating-cathode area is immersed in the electrolyte at one time; the remainder of the sheet is subject to re-solution of the zinc deposit by the adhering electrolyte. With disks of the required size, undue warping takes place, which results in the edge of the cathode coming in contact with the anode. Stripping the deposited zinc from rotating cathodes is a slow and expensive operation.

Starting sheets of zinc have been tried in place of aluminum depositing blanks, but have never proved successful. Thin deposits of zinc tear easily and, when dried, become quite brittle. The production, storage, and handling of zinc sheets is a difficult problem. Contacts between starting sheets and supporting bars cannot be made in a satisfactory manner. In operation the sheets tend to redissolve at the solution line, especially if the solution becomes slightly impure, causing the sheets to fall into the cells. The use of aluminum depositing blanks leaves little to be desired; they operate with so little trouble that no great incentive is given to the search for improved methods. The use of starting sheets would save in the cost of aluminum and would have some advantages because of the heavier sheet to be melted, but the experience so far with starting sheets has not been particularly encouraging.

If it becomes necessary to discard solution because of an overproduction of sulphate in roasting, the solution to be discarded should be depleted to less than 10 g. of zinc per liter. A separate group of cells should be used and a higher rate of flow than usual maintained in order to prevent overheating. The ampere efficiency on these cells will be much lower than normal, but the voltage will also be below average, and the actual loss in power will not be of any great consequence. Careful control of roasting conditions and a close cooperation among the various divisions of the plant, however, make it unnecessary to discard solution except under the most unusual conditions.

Melting and Casting.—Electrolytic zinc as cathode sheets has a very limited market. For most purposes the cathode sheets must be melted and cast into slabs. Melting must be done under carefully controlled conditions to prevent an excessive formation of dross. Casting of the molten zinc into slabs is a simple operation and can be done quite cheaply. The total cost of melting, casting, handling dross, and loading slabs for shipment amounts to only about 8 per cent of the total zinc production operating expenses, when hand labor is used for casting and loading.

A reverberatory furnace is commonly used for the melting operation. The depth of bath in zinc-melting furnaces is greater than is customary in similar furnaces for most other metals. The bath depth of the zinc-melting furnace varies from 30 to 36 in., depending on the area exposed for heating the bath. With a depth of 30 in., the hearth should be about 15 ft. wide by 20 ft. long. While, for construction purposes, a reverberatory furnace is commonly used, a furnace designed to transfer its heat to the bath from underneath would be better suited to the purpose than one heated through the surface of the bath. As much melting as possible is done under the surface of the bath. In the reverberatory furnace, the temperature must be carried so high to drive the necessary amount of heat into the bath that some burning of the zinc to zinc oxide is unavoidable.

The furnace is built on a steel pan to prevent possible loss of zinc through the furnace bottom. This steel pan is placed on concrete piers to allow a circulation of air under the furnace. The brick hearth is then built inside the pan. Common brick may be used for the bottom and hearth, but firebrick is necessary above the metal line and for the furnace roof. One or more charging holes, large enough to permit the passage of several cathode sheets, are built into the furnace roof. These holes are closed, except when charging the furnace, by remote-controlled cast-iron doors, usually water-cooled. Ladle wells, from which the zinc is ladled while casting, are built into one end of the furnace. These ladle wells are open on the bottom, and the sides extend below the surface of the bath to prevent dross from getting into the casting ladles, and to exclude air from the furnace. Doors are provided along the sides of the furnace, just above the metal line, for rabbling and skimming dross.

Casting is usually done by hand, using ladles carried from a trolley running on an overhead I beam. Each ladle holds a little over 200 lb. of molten zinc, which is enough to cast four slabs. The molds are made of cast iron, and the slabs cast in them each weigh 50 to 60 lb. The molds are placed on racks in a straight line under the I beam. Casting on a revolving wheel to carry the molds is not satisfactory because of the rough surface formed on the slabs by vibrations set up by the wheel. In order to obtain a bright smooth surface on the finished metal, the slabs are skimmed by hand as soon as they are poured. The slight film formed on the surface is removed by this skimming, along with any air bubbles during pouring. After the slabs are cast and skimmed, they are cooled by a water spray on the backs of the molds. As soon as the metal has "set," the molds, which are pivoted near the center, are turned over and the slabs dumped. The slabs are then stacked by hand and trammed away by either hand-drawn or powered trucks. A crew of three men can pour, skim, and stack 30 to 35 tons of zinc each working shift. With the larger furnaces, two or more ladle wells, ladles, and mold racks are usually provided.

Dross is skimmed from the furnace at regular periods into some suitable conveyance and is delivered either to a screening plant or to a "dross drum." In either case the object is to remove as much of the metallic zinc as possible from the dross. If the dross is to be screened, it is cooled before treatment; but if it is to be handled by a dross drum, it is delivered to the drum as hot as possible. The dross drum is a horizontal steel cylinder capable of being rotated on its longitudinal axis. The circumference of the drum is in the form of a modified scroll. When revolved in one direction, the charge is thoroughly mixed; but when the direction of the rotation is reversed, the drum empties itself. A drain at one end of the drum allows molten zinc, separated from the dross by action of the drum, to be drained off.

The metallic zinc recovered from dross is either returned to the melting furnaces or used for the production of zinc dust. This "treated" dross contains some mechanically held metal and also an appreciable amount of chlorine from the flux used in the furnace. The metallics must be oxidized and the chlorine reduced to a low figure before the dross can be returned to the leaching system. A separate furnace may be provided in which, by continued heating, the metallics are oxidized and most of the chlorine driven off. In many cases the dross can be sold as a separate product. Dross can also be reduced to zinc dust by reduction with coke in an electric furnace.

Furnace Operation.—Any fuel may be used with which a reasonable control of furnace atmosphere and temperature may be had. In order of preference, the fuels are gas, oil, and coal. A neutral or slightly reducing atmosphere should be maintained in the furnace to avoid burning the zinc. The temperature of the furnace gases should be kept below 600°C., preferably around 550°C.

Cathode sheets are charged into the bath of molten zinc through a charging door in either the roof or side of the furnace. As many sheets are charged at one time as

can be accommodated by the handling equipment and the bath of molten zinc. Some system such as rollers or slides is used so that the stack of cathodes can be charged with the least possible admission of air. As the stack of sheets falls into the bath, the individual sheets spread, allowing the molten zinc to pass around each sheet. If the furnace is large enough, more than one charging door may be provided, in order to spread the charge as much as possible. Ideally, the total charge should pass into the bath and out of contact with the furnace gases. Melting should take place under the surface of the bath. If the furnace is large enough, most of the heat necessary for melting is absorbed from the molten bath, which in turn receives its heat through the layer of dross on the surface of the bath. This ideal method of melting is seldom attained because of the large bath of metal necessary if 100 to 150 tons of cathode sheets is to be melted during each 24 hr. of furnace operation. In this case it becomes necessary to sacrifice some zinc by burning in order to maintain the necessary melting rate. Charging and casting are carried out simultaneously, and the level of the bath is held as constant as possible.

Some air is admitted into the furnace with each charging of cathode sheets, partially destroying the reducing atmosphere, and allowing a small portion of the zinc to burn with the formation of zinc oxide. A thin film of zinc sulphate is usually present on the surface of each cathode. The greater the amount of "sprouting" on the sheets, and the greater the porosity of the sheets—as when produced from an impure solution —the more air and zinc sulphate will be carried into the bath per pound of zinc. The zinc oxide produced in the furnace and the zinc sulphate from the sheets form a "dross" that rises and floats on the surface of the bath. This material holds within it a high percentage of metallic zinc and forms an insulating blanket that prevents efficient heat transfer to the bath. A small amount of dross on the surface of the bath is desirable as it protects the surface of the bath from further oxidation. The formation of a large amount, however, seriously affects the recovery of cathodes to slabs. Accumulations of dross in the furnace are removed at regular intervals. If the furnace is cooled down to prevent the burning of zinc and the dross is rabbled thoroughly, a large part of the metallic zinc held in the dross will drain into the bath. A small amount of sal ammoniac used as a flux aids in this separation by dissolving the oxide film surrounding the particles of zinc and allowing them to coalesce. An excessive amount of sal ammoniac should be avoided from the economic standpoint. Normal consumption of sal ammoniac is about 1 lb. per ton of cathodes melted. Rabbling also causes the formation of some oxide; the side doors must be open during the operation, admitting air to the charge; and a greater surface of zinc is exposed. After being thoroughly worked in this manner, and all the metallic zinc possible drained into the bath, the remaining dross is raked out through the side doors of the furnace. The dross is then either screened or treated in a dross drum. In the dross drum more sal ammoniac is added, and the resulting metallic zinc is allowed to drain out of the "dry" dross. A fairly complete separation is thus obtained, producing a dross containing about 80 to 85 per cent zinc. From 3 to 5 per cent of the weight of the cathode sheets charged goes into dross, the amount depending on the physical condition of the surface of the sheets, the crystalline structure of the metal, furnace operation, and the thoroughness with which the dross is treated for the recovery of metallic zinc. Less than 4 per cent dross is considered good work for average sheets. If the furnace capacity is exceeded, and it becomes necessary to melt a large part of the charge above the molten bath, it is almost impossible to prevent the formation of an excessive amount of dross.

Dross is a desirable source of zinc for lithopone, high-grade zinc oxide, and zinc chloride, much of it being used for these purposes. It is also a desirable material for some retort zinc smelters, requiring no roasting and enriching the lower grade zinc

materials treated. Its chlorine content is the only objection to returning it to the leaching division. If there is enough soluble silver in the calcine being treated to remove some chlorine from solution, roasting the dross at 400 to 500°C. will reduce its chlorine content sufficiently to permit re-treatment in the leaching division. If dross is to be re-treated, roasting, leaching, purification of solution, electrolysis, and melting of the resulting zinc must be charged against the amount of zinc recovered. Zinc dross may also be used for the production of zinc dust when reduced by suitable treatment in an electric furnace. Disposal of dross must be determined with respect to plant location and cost of re-treatment.

The flue gases from the casting furnaces carry a considerable amount of zinc oxide, which can be efficiently recovered by passing the gases through a baghouse. Cotton bags can be used if enough cooling pipes are used to cool the gases below 130°C. before entering the bags. The material caught is a mixture of zinc oxide and unburned carbon; it also contains an appreciable amount of chlorine from the sal ammoniac flux used in the furnace. This material can be disposed of in several ways: it can be water-leached to remove the chlorine and added to the leaching system, it can be added to the regular feed to the roasting furnaces, or it can be sold as a separate product.

Zinc Dust.—Zinc dust, for use in the purification of solution in the leaching division, is made by the atomization of molten zinc with compressed air. Molten zinc is transferred from the melting furnaces to a graphite crucible provided with a suitable heating arrangement to keep the zinc molten. The molten zinc, at a fairly high temperature, runs in small streams through holes in the bottom of the crucible, where it is immediately caught by a blast of compressed air, atomized, and blown into a settling chamber. The particles of zinc are cooled so rapidly that practically no oxidation takes place. Fineness of dust is controlled by air pressure, size of the stream of zinc, and the design and location of the air nozzle with respect to the stream of zinc.

The holes in the bottom of the crucible or pot, through which the molten zinc is carried to the air blast, are subject to a great deal of wear from the zinc stream. An increase in the size of the hole increases the size of zinc particles produced. It is therefore necessary to maintain as nearly as possible the original size of opening. This is accomplished by boring holes in the bottom of the crucible into which are cemented graphite plugs. These plugs are drilled for passage of the stream of molten zinc and are replaceable when the holes become too large. This results in a large saving in cost through a much longer crucible life.

The shape of the air jet formed by the nozzle or nozzles used in the atomization of zinc dust is of great importance in determining the efficiency of the operation. Multiple nozzles are much more satisfactory than a single opening. The air nozzles should form a jet which, if visible, would have the appearance of a U- or crescent-shaped trough in which the steam of molten zinc is caught. The bottom of the jet should be heavier than the sides. The air jet should converge to a point just beyond where struck by the molten zinc. If the stream of molten zinc strikes too far behind this point, some of the zinc will be carried up and out before becoming completely atomized; if too close to this point, the zinc stream will not be entrapped.

High air pressures give finer dust, but 75 lb. pressure will give a product most of which is finer than 100 mesh. The air supply to the jets must be well trapped to remove any oil carried over from the compressor; otherwise an explosion may occur in the dust-collecting system. Finely divided zinc dust in suspension is highly explosive, and particular care should be taken to keep open flames away from the dust plant.

If a classification of the zinc-dust particles is desired, sufficient air is drawn through the chamber into which the dust is blown to carry out the finer particles.

This fine dust is then caught by suitable collecting equipment. If no classification is desired, the chamber is vented through bags or other filtering equipment located over the chamber and discharging into it.

Zinc dust is usually produced only for local consumption, but is sometimes sold as a separate product. Because of the high purity and relative coarseness of the usual zinc dust made by electrolytic-zinc plants, it is not entirely satisfactory for use in cyanide plants.

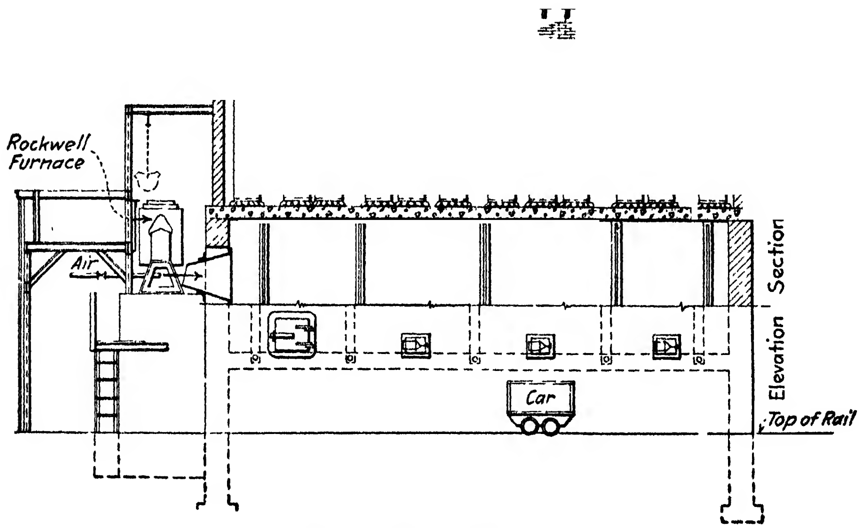

FIG. 14.—Zinc-dust plant

GENERAL PLANT DATA

Labor.—The total labor required for operation and maintenance, including everything from the unloading of the concentrate to the shipping of the finished zinc, will vary from 1.5 to 2.0 men per ton of zinc produced, depending on the capacity of the plant and the grade of concentrate treated. Low-grade concentrate requires more men in the roasting and leaching divisions, per ton of zinc produced, than high-grade concentrate. Increasing the capacity of a plant decreases the number of men required per ton of zinc. A high percentage of the labor required is what is usually termed unskilled labor. Working conditions are such that a good class of labor is attracted.

Power.—The actual power required for deposition of zinc at 30 amp. per sq. ft. will average about 1.5 kw.-hr. direct current per pound of zinc. Assuming 93 per cent conversion efficiency from alternating to direct current, approximately 1.6 kw.-hr. alternating current will be required per pound of zinc. This is 3200 kw.-hr. per ton of zinc. Auxiliary power for the roasters, leaching plant, casting, compressed air, etc., varies in its relation to the power for the electrolyzing cells with the size of the plant and the grade of concentrate being treated. For a plant producing 100 tons of zinc per day from a 50 per cent concentrate, the auxiliary power will amount to less than 10 per cent of the total power. This proportion of auxiliary power decreases as the size of the plant increases. Assuming 10 per cent for auxiliary power, the total power requirement for a 100-ton plant will be 3560 kw.-hr. per ton of

zinc, or a total of 15,000 kw. required. Decreasing the current density decreases the total power requirement slightly.

Auxiliary Equipment.—Leaching in 30-ton Pachuca tanks requires 125 to 150 cu. ft. of free air per minute per tank. This air is supplied at 20 to 30 lb. pressure. Some air is also required for agitation of pulp in filters, opening of thickener spigot lines, and various other purposes. It is desirable that air higher than 30 lb. per sq. in. should be furnished for these purposes. The manufacture of zinc dust requires an air pressure of at least 75 lb. per sq. in. The volume of air required for zinc-dust manufacture depends on the number of nozzles and the size of the stream being atomized. For all purposes, an average 100-ton plant should have a capacity of at least 1000 cu. ft. of high-pressure air per minute.

Some steam is used for heating solution in the leaching plant, in addition to the amount normally required for heating various buildings. The amount required for heating buildings will depend on climatic conditions and the type of building construction. Some heat is generated in the leaching tanks, the temperature averaging 50°C. or higher, and the large area exposed by the surface of the thickeners allows much of this heat to be radiated. This reduces the amount of steam heating necessary in the leaching plant. A similar condition exists in the electrolyzing division, but not much of this heat can be conserved because of the amount of ventilation required. No extra heat is required in the roasting and casting divisions beyond that needed to keep the air and water lines from freezing.

Water is required in increasingly large quantities, as the current density is increased, for cooling the cells. If the plant is so arranged as to permit proper distribution, the water for cooling the cells may be used again for all the other requirements of the plant. The only exception to this is the water used for cooling the transformers. The cell requirement—6 to 8 gal. per min. per ton of zinc daily output—is more than sufficient in volume for the other requirements. If reasonable care is taken of the cooling apparatus in the cells, the water will not be contaminated from this source.

A small foundry for making copper, bronze, and lead castings of spare parts, for replacement of equipment in contact with corrosive solutions, is almost a necessary adjunct to an electrolytic-zinc plant. It will prove to be a highly profitable investment. Carpenter, pipe, boiler, blacksmith, electric, and machine shops are needed to build and install new equipment and to care for the regular maintenance work.

First Cost of Plant.—The first cost of an electrolytic-zinc plant, including all auxiliary departments, water system, tramming systems, bins, etc., will vary from $30,000 to $40,000 per ton of daily zinc capacity. The cost depends on the size of the plant, type of construction, cost of labor and supplies, and the location of the plant. A large plant built under the most favorable conditions would probably cost about $30,000 per ton of daily zinc output. A plant of only one-half the capacity of the larger, under the same conditions, would probably cost $35,000 to $40,000 per ton. Power-conversion equipment and motors make up the largest single item of cost. The second largest item is made up of electrolytic-cell equipment, such as aluminum cathodes, lead anodes, cooling coils, tank linings, copper bus bars, conductor bars, and other items made of copper or lead. Much of the leaching equipment is of copper, lead, or bronze. Roasting and leaching equipment is almost all of standard design and, for this reason, has a higher salvage value than if made specially for individual applications.

The first cost of an electrolytic-zinc plant depends less on the grade of material treated than that of a retort plant. The electrolyzing division and the melting and casting division are altogether dependent on the amount of zinc produced regardless of the source. Much leaching-plant equipment is dependent on the volume of solu-

tion to be handled and, therefore, on the zinc output. The roasting equipment necessary is largely dependent on the grade of concentrate. This is also true, to a large extent, of some of the leaching-plant equipment. The roasting equipment required for a given zinc production is roughly inversely proportional to the grade of zinc concentrate treated. The first cost of a plant of this kind, therefore, decreases as the grade of concentrate increases.

Recoveries.—If adequate means are provided to collect the dust from the roasting furnaces, the total losses in the roasting division will be almost negligible. The amount of dust carried out of the furnaces by the flue gases is usually high when roasting flotation concentrates in multiple-hearth furnaces, but is mostly a circulating load when proper equipment is used. The only other source of loss in the roasting department is through screening and cooling of the calcine and in crushing oversize calcine preparatory to returning it for further roasting.

The leaching-plant residue contains unroasted zinc sulphide from the calcine, zinc ferrite insoluble in the leaching process, some zinc oxide not dissolved in the leaching solution, and any zinc sulphate not removed when the residue is washed with water. The total loss of zinc as residue is the largest single loss of the electrolytic process and may account for as much as 20 per cent of the total zinc with a particularly unfavorable zinc ore. The loss of zinc as ferrite is usually the main part of the residue loss. In case of very pure ores, however, the loss of zinc as sulphide may exceed the loss as ferrite. Any unroasted zinc sulphide carries approximately twice as much zinc as sulphur. A 0.2 per cent sulphide sulphur in the calcine, therefore, will mean a loss of 0.4 per cent zinc, which is equivalent to 1 per cent of the total zinc in a 40 per cent concentrate. A concentrate containing much iron will produce a correspondingly high percentage of residue with a large loss of zinc as ferrite. As has been previously pointed out under the discussion of the formation of ferrite, the amount of ferrite formed cannot be definitely predicted from an analysis of the concentrate because of the fact that the intimacy of contact between the particles of zinc and iron influences the completeness of combination. It can be assumed for general purposes, however, that as the iron content of the concentrate increases, the amount of zinc ferrite loss in the residue also increases. The real measure of efficiency of the leaching process is shown by the amount of undissolved zinc oxide remaining in the residue; good operation requires that the amount of such zinc in the residue should be less than 5 per cent of the total zinc in the residue. When treating a concentrate containing approximately 55 per cent zinc, the total zinc in the residue should not be more than 6 per cent of the zinc in the concentrate; of this amount, 8 per cent—or about 0.5 per cent of the zinc in the concentrate—will be present in the residue as zinc oxide. The amount of zinc lost in the residue as zinc sulphate will be approximately twice that lost as zinc oxide. In other words, about 10 to 20 per cent of the total zinc in the residue, or about 1 per cent of the zinc in the original concentrate, will be lost in the residue as zinc sulphate. The normal zinc loss in residue from a high-grade concentrate containing 55 per cent zinc may be summed up as follows: 0.2 per cent of the sulphur unroasted will cause a loss of 0.7 per cent, undissolved zinc oxide will cause a loss of 0.5 per cent, zinc sulphate not washed from the residue will cause a loss of 1 per cent, and the insoluble ferrite will cause a loss of approximately 3.8 per cent. This is a total loss of 6 per cent. As the zinc content of the concentrate decreases, with a corresponding increase in the iron content, the percentage loss from sulphide and ferrite will increase, and the percentage loss as zinc oxide and zinc sulphate will decrease. With a concentrate containing 40 per cent zinc, the residue loss will amount to about 12 per cent of the total zinc.

Figure 15 gives a formula for determining leaching recovery (recovery from calcine to residue). It is based on the fact that the amount of zinc in a definite amount of

calcine that is insoluble in 1 per cent H_2SO_4 equals the amount of such insoluble zinc in the residue produced from this calcine. The recovery calculated from this graphic formula does not include any loss in purification residue.

The amount of purification residue produced and the amount of zinc in such residue depend mainly on the amount of copper and cadmium in the solution to be purified, and therefore on the amount of zinc dust used for purification of solution. The purification residue also contains some basic sulphate precipitated from the solution, and solids overflowing the neutral thickeners. The amount of zinc from these sources makes the zinc content of this residue approximately equal to the

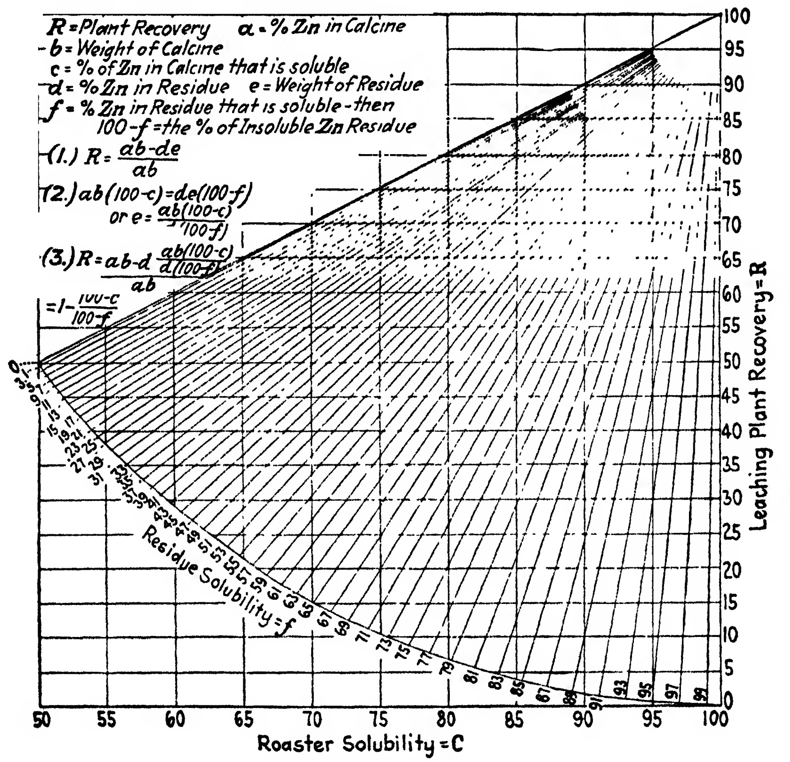

FIG. 15.—Graphic zinc-recovery formula (based on fact that insoluble zinc in calcine equals insoluble zinc in residue).

amount of zinc dust used for purification. Treatment of the purification residue for the recovery of the zinc and separation of the copper and cadmium will recover 90 to 95 per cent of the zinc content. With adequate treatment, the net loss of zinc from this source should not be more than 10 per cent of the zinc dust used.

There is no loss of zinc in the electrolyzing division, other than that from mist or spray from the surface of the cells, unless acid is discarded. With careful control of roasting and leaching operations, there is really no necessity for discarding acid. Even if it does become necessary for a plant to discard some acid, the loss of zinc from this source can be minimized by depleting the zinc in this solution to 1 per cent or less.

If the dust in furnace gases is properly collected, there should be practically no zinc loss in the melting and casting division. The only loss in this case is a result of handling and treating the collected dust and the zinc dross produced by the melting

operation. The total loss in this division should not be more than 0.10 per cent of the total zinc entering the plant.

There is always some loss of zinc through handling solution and calcine. The total loss from handling should not be much; the amount depends on the arrangement of the plant divisions and on the provisions for handling occasional spills of solution. The sum of all such losses in the leaching and electrolyzing divisions should not exceed 1.0 per cent of the total zinc loss.

Starting with a concentrate containing approximately 55 per cent zinc, 0.6 per cent copper, and 2 per cent iron, the expected losses should be about as follows: roasting, 0.75 per cent; leaching-plant residue, 6.0 per cent; purification residue, 0.25 per cent; melting and casting division, 0.10 per cent; general handling, 1.0 per cent; total, 8.1 per cent. This is an over-all recovery of 91.9 per cent from concentrate to finished zinc.

By-products.—The location of the plant with respect to markets for the sale of by-products limits the value and the production of these materials. Common by-products, which may be produced in connection with regular plant operation, are sulphuric acid, zinc dust, zinc oxide, lithopone, zinc salts, cadmium, and cadmium salts.

Sulphuric acid can be profitably produced from the roaster gas of an electrolytic-zinc plant if a satisfactory market exists for this product. When high-iron concentrates are to be treated, however, close temperature control is required and the upper hearths of the furnace must be kept cool by the admission of air to prevent the formation of an excessive amount of ferrite. A condition such as this renders the production of sulphuric acid unprofitable unless the value of the by-product is such that it is cheaper to provide some special method of residue treatment to recover the zinc combined as ferrite and to produce acid from the roaster gas.

Some sulphuric acid is produced by sulphate roasting and the subsequent electrolysis of the resulting zinc sulphate. More or less zinc sulphate is formed depending on the conditions of roasting. Also, if the iron sulphate formed during roasting is not decomposed in the lower part of the furnace, the SO_4 radical will unite with zinc to form zinc sulphate during the reactions in the neutral leach by which iron hydroxide is precipitated with excess zinc oxide. This is a source of sulphuric acid; but acid is expensive to produce in this manner, as the spent electrolyte must be evaporated in order to obtain a marketable product. If, however, a market is also available for lithopone or zinc sulphate, such acid can be profitably utilized.

Zinc dust is produced primarily for the purification of solution. The high purity and relative coarseness of the dust normally used for this purpose makes it undesirable for market purposes. There is no objection to the use of dust containing some lead and cadmium in the regular zinc-dust purification. Therefore, if a suitable market exists, it is very easy to lower the purity of the dust produced without affecting the efficiency of the dust used for local consumption. The dust can also be produced in any desired degree of fineness by slight changes in the atomizing process and by classifying the dust while it is being collected.

Zinc dross is very often sold as a by-product of the electrolytic-zinc process. Much of it has been used in the production of lithopone, high-grade zinc oxide, and for zinc chloride. Zinc dross is also a desirable material for some retort smelters as it is very high in zinc content and requires no preliminary treatment. Whether zinc dross is sold as a by-product or re-treated for the production of zinc depends on the location of the plant and the existing markets.

Zinc sulphate solution suitable for electrolysis is of a high degree of purity except for manganese. When manganese has been removed by the usual methods, the resulting solution is of exceptional purity and is highly desirable for the production

of lithopone. The acid combined with the zinc costs practically nothing to produce, and the zinc may be figured to be worth the market price at the plant less the cost of electrolysis, melting, and casting. If the plant considering the sale of zinc sulphate for this purpose regularly discards acid from the system, the production of lithopone, in an amount just sufficient to offset the necessary depletion in acid content, could be credited with the saving in power and zinc loss resulting from the discarding of acid. Zinc sulphate can be produced by the evaporation of regular plant solution.

Cadmium metal has become one of the main by-products of the electrolytic-zinc process. Practically all ores of zinc contain small quantities of cadmium. In the metallurgy of zinc it is necessary to remove the cadmium from the solution previous to electrolysis if high-grade zinc is to be produced. The cadmium is first eliminated from the regular zinc cycle in the purification residue. During the treatment of purification residue for the recovery of zinc and copper, the cadmium is usually precipitated from solution as an impure sponge metal. From this state it is but a simple process to produce cadmium metal suitable for market. A further advantage in producing cadmium as a by-product of the electrolytic-zinc process is that the main portion of the expense is borne by the zinc plant.

The impure cadmium sponge is stored in stock piles for several days to allow partial but not complete oxidation. This process of oxidation may be speeded up by piling the sponge on a large heated pipe. Unoxidized cadmium sponge is slow to dissolve in dilute sulphuric acid, but when oxidized it will dissolve very rapidly. The oxidized sponge contains zinc, lead, iron, cobalt, nickel, and sometimes thallium as impurities. All these, with the exception of zinc, must be removed previous to electrolysis of the cadmium solution. The sponge is dissolved in return electrolyte from the cadmium electrolyzing cells, in spent electrolyte from the zinc cells which have been depleted in zinc, in commercial sulphuric acid diluted with water, or, as is quite often the case, in some combination of these acids. The leach is neutralized with a large excess of the incompletely oxidized cadmium sponge and, owing to the presence of some metallic cadmium, most of the impurities are eliminated by replacement with cadmium. The leach is then filtered, and if necessary, further purification steps are carried out to eliminate any especially troublesome impurities still present. The solution after purification, for best results, should contain 180 to 220 g. per l. of cadmium. The solution may also contain zinc in an amount not to exceed 50 per cent of the cadmium content without detrimental effects to the electrolysis of cadmium.

Cadmium is difficult to electrolyze because of the formation of trees and sprouts. The formation of trees and sprouts can be minimized by keeping the cadmium content in the electrolyte relatively high. The cell and electrodes in the cadmium electrolysis cell are practically the same as in the regular zinc cell. The cells are fed with solution individually and are not in cascade. Glue is added to prevent the excessive formation of beads. The current density used in the cadmium cell ranges between 2 and 15 amp. per sq. ft.

The deposited cadmium metal is stripped from the cathodes each day and rolled into bundles for melting. The bundles are melted under a layer of caustic (NaOH) in large iron pots, and cast into slabs weighing approximately 75 lb. each. These slabs are remelted and cast into shapes for market. The usual shapes are balls, pencils, slabs, or special anodes.

Residue Treatment.—Leaching-plant residue as discharged from the filters contains a high percentage of moisture. The moisture content varies from 20 to 35 per cent according to the amount of gelatinous material precipitated in the neutral leach, during the purification of iron, silica, alumina, etc., in comparison with the amount of sandy material in the residue. The presence of relatively coarse material is of considerable benefit in the filtering and washing operations and aids in producing a

low moisture content by keeping the cake "open" to passage of the solution and wash water. High-grade zinc concentrate produces a residue high in moisture because the amount of gelatinous material produced from such a concentrate is high in proportion to the amount of sandy material in the residue. As a general rule, the amount of sandy material increases as the zinc content of the concentrate decreases. To be suitable for the usual methods of treatment, the residue must be dried further to reduce the moisture content.

A direct-fired rotary drier has a large capacity and is cheap to operate, and is superior in these respects to other types of drying equipment. It consists of a brick-lined steel tube mounted on rollers at a slight incline and revolved by a gear-and-pinion drive. The material to be dried is introduced through a chute at the upper end and, because of the revolution of the inclined tube, slowly passes through the drier to the lower end where it is discharged. The tube is fired at the discharge end, and the hot gases leave the drier at the feed end.

Part of the drying is done by contact between the residue and the hot gases and part by contact between the residue and brick lining. The lining is exposed to the hot gases for more than half of the revolution and absorbs heat that is later transferred to the residue. The revolving motion of the drier carries the residue part way up the side of the tube in the direction of rotation, and then the material falls or rolls back into the trough. A good contact between the residue and the hot gases is given because of this action. The rolling action of the drier gives a product that is formed into small lumps or balls. This product can be handled without excessive dusting loss and does not tend to hang up in bins or hoppers. The dried material contains 10 to 15 per cent moisture. The apparently high moisture content is due to incomplete drying in the centers of the lumps. Further reduction in the moisture content is not desirable with this type of drier, as an excessive dust loss from the driers and in handling would result; if a lower moisture content is necessary, some other type of drier should be used.

The methods of treating the final residue from the electrolytic-zinc process are many and varied. Lead-furnace or copper-furnace treatment of the residue, or a combination of the two, is the usual procedure if the zinc plant is situated in a locality where these methods are economically available. Some wet methods have been employed in the past for residue treatment but, as they are not entirely satisfactory, are not now in common use. The margin of profit in treating the final residue is so low that not many special methods have been developed; several methods have, however, been adapted from other metallurgical process. Among these several methods are the Waelz process, the ash-fusion process, and the electrothermic process.

Classes of Residue.—Residue may be divided into four general classes: (1) that containing insufficient values to pay for the cost of further treatment; (2) that containing lead as the only value of consequence in deciding the method of treatment; (3) that in which metals other than lead are present in considerable amounts, but in which lead is in excess of copper in value; and (4) that in which the value of recoverable copper exceeds the value of recoverable lead.

The residue from class 1 is a waste product and may be discarded by countercurrent washing and sluicing. This method of disposal will save some of the cost of filtering and repulping. The difference in cost between countercurrent washing and the usual filtering and washing operation offsets the loss of value in the residue. The economics of the two methods for the disposal of a class 1 residue must be considered in the light of local plant conditions before deciding which is the most desirable method for any individual situation. The point at which to draw the line between a class 1 and a class 2 residue must also be decided by local conditions.

A residue in class 2 is one that contains lead as the only value of consequence in deciding the method of treatment. A residue of this class may be treated in a lead blast furnace, in an ash-fusion gas producer, by the Waelz process, or by various wet methods. The location of the zinc plant with respect to an established lead-smelting plant, the desirability of the particular residue as a feed to the lead plant, and other local conditions will decide the most economical method of treatment.

Leaching with a saturated solution of common salt will recover over 90 per cent of the lead from a residue containing 10 to 12 per cent lead, but will give a comparatively low recovery of silver. Only a short leaching period is required, the leach settles rapidly, and the solution is clear enough to electrolyze without further clarification. Lead is electrolyzed with iron anodes and cathodes; the iron consumption amounts to 0.3 lb. per pound of lead produced. From 12 to 15 lb. of lead is produced per kilowatt-hour. The deposited lead is very spongy and contains about 80 per cent lead when dried. The spongy lead forms a large amount of dross since it oxidizes rapidly in contact with air. The process is really one of concentration rather than a direct reduction of lead, but the low cost of equipment and the high recovery of lead makes this method very attractive for this class of material.

The residue in class 3 is one in which other metals besides lead are present in considerable amounts, but in which lead is in excess of copper in value. The treatment of a residue in this class is usually a straight lead-smelting operation. The low recovery of copper, silver, and gold eliminates the simple brine leach except under especially unfavorable conditions for lead smelting. A considerable amount of work has been done to develop wet methods for the extraction of values from class 3 residues. Several of these wet methods have been tested, but in practically all cases they have been discarded in favor of other methods of treatment. The Waelz process, the ash-fusion gas-producer process, and the electrothermic process are applicable to the treatment of the residue in this class.

Some residue that will fall into class 3 contains scarcely enough lead to pay the freight and the cost of treatment at a lead smelter, but does contain enough silver, gold, and copper to make it a valuable product. Such a residue may be smelted in a reverberatory furnace, with suitable fluxes and reducing material, and a copper matte produced that contains most of the silver and gold. The fume from this furnace will contain a high percentage of lead. This lead can be recovered in a lead smelter. The matte can then be treated in a converter to recover copper, gold, and silver as in the regular production of blister copper. Some lead is reduced to the metallic state in the reverberatory furnace and leaves the furnace with the copper matte. This lead, if in a considerable amount, may be either separated from the matte, or collected as a fume from the converter. The zinc in the residue treated in the reverberatory furnace is largely absorbed by the reverberatory slag, but some is collected with the lead fume. Copper concentrate, or some other sulphur-bearing material for matte formation, limestone, crushed coal, and siliceous ore (if silica is needed) are mixed with the residue to make up the reverberatory charge. Slag containing 30 per cent SiO_2, 30 per cent FeO, and 16 per cent CaO has been found to carry the least lead and copper and to absorb the most zinc of any of a series covering a wide variation of analyses. Such a slag will normally contain less than 2 per cent lead and over 12 per cent ZnO when treating a residue containing 12 per cent lead and 12 per cent zinc. The amount of screened coal required in the charge is about 4 per cent of the weight of the residue.

A residue in class 4 is one in which the value of the recoverable copper in the residue exceeds that of the lead. Such a residue may be treated in a reverberatory furnace as just described. If the amount of lead in the residue is not high enough to justify the formation of a type of slag to ensure its elimination and the collection of the lead

as fume, the residue may then be advantageously treated in a copper blast furnace or copper reverberatory.

A combination reverberatory and lead blast-furnace method of treatment is especially well adapted to the treatment of residue containing some copper, an appreciable amount of zinc, and not enough lead to make a direct lead blast-furnace treatment economically feasible. Part of the residue may be smelted in a reverberatory furnace and the copper and most of the zinc eliminated in the matte and slag. The fume from this operation, high in lead and low in zinc and copper, can then be added to the remainder of the residue to make up a blast-furnace charge. In this manner the amount of zinc to be slagged in the blast-furnace operation is materially lowered, which reduces the amount of slag formed, and the percentage of lead recovered is greater.

Before zinc-plant residue can be treated in a blast furnace, some form of agglomeration must be resorted to, or the dusting losses will be prohibitive. A fair sinter may be made by mixing the residue with foul slag and coal and putting the mixture over a Dwight-Lloyd machine. It may also be formed into briquettes, without the addition of any other material, which are hard enough so that they may be handled without producing much dust. Fume added to the residue hardens the briquettes, and this additional hardness may be found advantageous if the residue is treated by the combination reverberatory and blast-furnace method. The briquettes may be formed by feeding partly dried residue into a pugmill where just the right amount of water is added to produce a mixture of the proper consistency. This product is then put through an auger brick machine and the resulting ribbon cut into blocks of suitable size. These blocks are then dried. The zinc sulphate and gelatinous material contained in the residue give the material sufficient binding properties to make a good hard briquette.

It is possible to eliminate zinc as a fume, in the reverberatory furnace, but the cost of treatment and the cost of subsequent purification of the solution produced from such a fume is high enough to offset the value of the zinc recovered. Arsenic, antimony, etc., are carried with the zinc fume, and when the fume is leached the solution is so impure that special methods must be used to prepare it for electrolysis.

The Waelz process is a relatively cheap method for the concentration of zinc from low-grade material and is used extensively all over the world. The Waelz process is especially adaptable to the recovery of metals from zinc-plant residues of all classes containing enough values to pay for the cost of treatment. The object of the process is to drive off zinc, lead, and other easily volatilized metals and to concentrate them as a fume. This fume is then treated for recovery of these metals. The kiln residue contains the nonvolatilizable metals and, if sufficient values are present, can be treated for their recovery.

The Waelz process requires no preliminary drying of the residue as slimes containing as high as 40 per cent moisture can be easily treated. The feed is simply mixed with the required amount of coke and fed to the kiln. Almost any sort of coke can be used. The charge is weighed and mixed in any simple sort of mixing machine and fed to the kiln through an inclined chute.

The kiln is a long, horizontally inclined cylinder with a brick-lined steel shell supported on riding rings and rollers. The usual slope of the inclined cylinder is 1 to 6 per cent of the length of the kiln. The kiln is rotated by a pinion driving a large toothed gear fastened around the circumference of the shell. A variable-speed motor is preferred on the larger installations. Some sort of stand-by equipment should be provided to operate the kiln in case the usual source of power fails.

The kiln is fired at the lower or discharge end of the inclined cylinder, and the waste gases are carried away at the feed end. The normal operating temperature

of the kiln is 1100 to 1200°C. at the fire end, and 500 to 600°C. at the exit point of the gases. The kiln is normally operated under induced draft produced by a fan in the collecting system.

The material to be treated is introduced through a chute at the upper end of the inclined cylinder. The rotating motion of the kiln causes the charge to be carried part way up the side of the cylinder in the direction of rotation. From this point it tumbles back into the trough at the bottom. The tumbling action of the charge, together with the incline of the cylinder, causes the charge to work its way slowly down the length of the kiln to the discharge end. The charge moves in a direction opposite to the gas flow. The moisture is evaporated, and the charge absorbs heat both from intimate contact with the hot gases and from contact with the heated lining. The maximum temperature allowable in the kiln is the softening point of the material treated. If the charge softens and begins to slag, all reactions stop immediately. The success of the Waelz process depends on the long period of reduction and on the fact that the reducing and oxidizing zones are actually superimposed on each other throughout the greater part of the kiln.

The fume and dust carried away from the kiln by the hot gases pass through settling chambers and collectors where the dust is settled out. The dust is much heavier than the fume and can be efficiently separated from it. The dust is usually returned to the kiln along with the regular charge. The fume and hot gases are lowered in temperature by passing them through cooling pipes, and the fume is collected in a baghouse or a Cottrell precipitator.

The kiln residue is discharged into any suitable container and is disposed of according to the value of the recoverable metal.

The treatment of zinc-plant residue by the ash-fusion gas-producer method was developed by the Société des Houillères de Saint-Etienne. It has been in use for several years by the Viviez works of the Société de la Vieille-Montagne. The Viviez electrolytic-zinc plant is too far from a lead smelter to make it possible to treat the residue economically by a lead-furnace operation.

The zinc-plant residue as delivered from the filters is first dried to about 5 to 6 per cent moisture in a rotary drier. The product from the drier is slightly moistened with water in a mixing machine and briquetted. The briquettes are further dried to produce a hard firm surface that can be handled without excessive mechanical loss.

The briquettes are added to the furnace along with salt cake and the various necessary fluxes. The slag formed contains about 30 to 34 per cent SiO_2, 18 to 24 per cent CaO, and 18 to 20 per cent FeO. A slag of this composition will contain a maximum amount of iron with a minimum amount of zinc. The matte produced by this process contains some of the iron and most of the copper, silver, and gold in the original residue. Certain other elements such as cobalt, nickel, manganese, arsenic, and antimony are also eliminated with the matte.

The gas produced by the apparatus carries off the volatilizable metals as a fume. A considerable amount of fine dust also accompanies the flue gases and is collected separately from the fume. The fume is cooled and collected by standard methods and is returned to the electrolytic cycle.

Recovery of Zinc from Lead Blast-furnace Slag.—Zinc can be recovered from lead blast-furnace slag by suitable treatment in a reduction furnace from which the zinc is collected as a fume. The method used at the East Helena slag-treating plant of the Anaconda Copper Mining Co., and elsewhere, has an advantage over most previous methods in that it is able to treat the molten slag direct from the blast furnaces, thereby saving the cost of remelting. It has the further advantage of being able to melt cold slag more cheaply than by treating back through a blast furnace, as pul-

verized coal is used for heating, and the melting and reduction processes are carried on almost simultaneously in the same furnace.

The plant consists of a slag-treating furnace, steel pipes for cooling the fume and gases, and a baghouse for collecting the fume. The furnace is rectangular in cross section, the sides, ends, and top of the furnace are jacketed for water-cooling, and the furnace bottom is a water-cooled cast-iron plate resting on a concrete foundation. Air and coal dust are admitted through tuyères along each side of the furnace, the slag is introduced into the furnace through a charge hole in one end, and the gases and fume are taken off from the opposite end of the furnace. The hot gases and fume are cooled by passing through steel cooling pipes and are filtered through woolen bags in the baghouse for recovery of the fume. The fume collects in hoppers underneath the bags and is drawn from the hoppers into railroad cars for shipment to the electrolytic-zinc plant at Great Falls.

A furnace charge consists of approximately 35 tons of slag. Slag, containing about 10 per cent zinc, is brought to the furnace in pots and is charged into the furnace by raising the pots by a crane and pouring the contents through the charge hole. Blowing is started, and more molten slag and crushed slag skulls are added until the full charge is in the furnace. The percentage of skulls used will vary with operating conditions of the lead blast furnaces, but normally does not exceed 30 per cent of the slag treated. If sufficient molten slag is available, no skulls are treated.

With all molten slag, a furnace cycle is about 30 min. for charging and 140 min. for blowing and discharging. Eight or nine charges can be treated per 24 hr. When skulls or cold slag are treated, the cycle is increased by lengthening the charging and melting period, while the blowing time remains nearly constant.

The zinc elimination is slow until the temperature of the charge has been brought up to around 1050 to 1100°C. After reaching the required temperature, the elimination of zinc proceeds at a fairly constant rate until the zinc content of the slag is reduced to about 3 per cent, when there is a marked slowing down in the rate of reduction. From 80 to 85 per cent elimination of zinc in the slag can be obtained within a 2-hr. blowing period, but this elimination may be increased to over 90 per cent by a longer blowing time. This, however, requires an excessive amount of coal for the amount of zinc eliminated and also reduces the capacity of the furnace. The most efficient period of blowing and the percentage of zinc recovery are determined by the operating conditions and by the value of the zinc recovered.

The consumption of coal in the slag-treating furnace varies from 20 to 30 per cent of the weight of the slag treated when 10,000 B.t.u. coal is used. Air consumption averages about 8000 cu. ft. of free air per minute and is introduced into the furnace under a pressure of 14 lb. per sq. in. Most of the fume comes off during the early part of the blowing period. Fume produced at East Helena averages about 70 per cent zinc and 6 to 7 per cent lead.

CHAPTER XV

PYROMETALLURGY OF ZINC[1]

By W. R. Ingalls[2]

Scope of Chapter.—My contribution to the first edition of "Handbook of Nonferrous Metallurgy" edited by D. M. Liddell was written in 1925, which was just prior to the general introduction of the process of preferential, or selective, flotation, which by fine grinding made it possible to separate the constituent minerals of almost any kind of mixed sulphide ore, resulting in the liquidation of many great ore deposits previously not of commercial value and bringing to the metallurgists great supplies of very fine ore (so fine as to pass a 200-mesh screen) and introducing new problems in metallurgical treatment. Furthermore, the efficiency of the flotation process was so improved that the grade of the concentrates was raised to upward of 50 per cent in zinc content, with less than 2.5 per cent in lead content, so that the zinc metallurgists were no longer much concerned over lead recovery, deleading having then been done in the mills, where it could be done more efficiently than in the metallurgical works.

The metallurgical problems were solved by the introduction of improved methods of handling, dust catching, and roasting, more particularly desulphurization, in which the introduction of the sintering process played an important part.

The zinc smelters were thus constrained to modernize their plants in these ways, at great cost. Soon, following such modernization, came the introduction of the New Jersey Zinc Co.'s process of distilling continuously in vertical retorts and the continuous electrothermic process of the St. Joseph Lead Co.

Further innovations were the process of refining crude spelter by fractional distillation, invented and introduced by the New Jersey Zinc Co., enabling the distiller to produce zinc of 0.9999 fineness, which was required in the die-casting industry that had been growing by leaps and bounds, and which had previously been supplied by the electrolytic zinc producers by superrefining of their solutions and the use of silver-lead anodes. Another innovation in practice, although it was not new in conception, was the more general dezinking of slags and retort residues by burning the zinc out of them either by the Waelz furnace or otherwise and returning the zinc oxide fume to further processing, which made possible nearly 100 per cent extraction of the zinc from most ores, although of course at additional cost.

Since 1925, the old process of intermittent zinc distillation has survived by virtue of improvements, but there has been no new plant of this type built, except Dumas in Texas. The zinc-distilling plants of the United States using natural gas as fuel have survived, contrary to expectations 15 years ago, but their fuel cost has increased. Additional zinc-smelting capacity during the last 15 years has been either through the continuous-distilling process, or more importantly through further extension of the use of the electrolytic process. The latter has been introduced in places as remote as Broken Hill in Northern Rhodesia, at Flin Flon in Manitoba, and at Cerro de

[1] This paper is a revision of the author's contribution to the Rocky Mountain volume of the American Institute of Mining and Metallurgical Engineers.

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Pasco, high in the Andes of Peru, under conditions where beneficiation by reduction and distilling would be unimaginable. At the present time, we do not foresee further extension of the old process of zinc smelting, although we contemplate its survival.

In view of these radical changes in the art, it appeared best not to undertake to revise the contribution of 1925, but rather to make use of my paper under the title of Intermittent Zinc Distilling from Ore that was published in the Rocky Mountain volume of the American Institute of Mining and Metallurgical Engineers. The privilege of free use of this copyrighted article was generously granted by the A.I.M.E.

The article is now condensed somewhat and also amended it in such ways as have been necessary to bring it up to date. Moreover, the sections on continuous distilling and the processes broader in scope and defined as zinc burning are new.

Some of the preliminary sections describing the travel of zinc ore up to and through the processes of desulphurization of course apply to the whole range of zinc pyrometallurgy and also of its electrometallurgy.

Unloading and Handling Concentrates.—The millman de-waters the flotation concentrate as much as possible, especially to save freight, but it comes to the metallurgist as a stiff mud containing about 10 per cent water. In winter it may freeze in the railway cars, which may have to be passed through a thaw house in order to permit unloading. This may increase materially the cost of unloading as an annual average. In the Middle West a brick house accommodating two box cars will thaw their contents in 24 hr. with the use of 3000 lb. of coal. Under prewar conditions, unloading by hand cost about 12 to 13 cents per ton; it was reduced to 6c. by mechanical unloaders, and raised to 40c. when the ore came frozen, which in a year might be to the extent of 10 per cent.

Ore Storage.—Zinc metallurgists who operate plants in close proximity to their ore supply, especially if the latter is a single mine, require less storage capacity than those situated remotely from the ore supply, and especially those who receive ores from many sources. The arrangements for unloading ore, storing it, etc., are not essentially different from those obtaining in the metallurgy of copper and lead. Whenever the desirability of a mixture is indicated, it is generally accomplished by drawing from separate bins.

Drying.—Flotation concentrates, arriving with about 10 per cent moisture, have to be dried and screened, and perhaps comminuted to break up lumps. In American practice revolving cylinders, internally heated, are used for drying. Plate driers of the Lowden type are also used. For screening, the vibrating sieve is used. Dust loss and other difficulties are obviated if the drying is performed only to reduce the moisture content to 3 or 4 per cent, in which condition the ore is easily handled, letting the drying be finished by spreading the ore on top of the roasting furnace (see Chaps. II, III, and V).

Roasting.—In American practice the Ropp mechanical furnace continues in use among the zinc smelters of the natural-gas fields. Among the zinc smelters which make sulphuric acid as a by-product there are survivals of the Hegeler furnace. However, in all the modernized plants the roasting is now done with circular furnaces of the McDougall type, such as the Wedge, Herreshoff, Skinner, and Warner-Ingalls. These furnaces are built with hearths of about 20 ft. diameter inside and 7 to 16 hearths in height, the larger of these furnaces roasting as much as 50 tons per day to complete desulphurization (much more than that if the desulphurization is not carried down so far) and delivering gas containing 5 per cent sulphur dioxide.

In Europe, furnaces of the McDougall type are also in use, but in general the European roasting is done in Spirlet (mechanical) and Delplace (hand-raked) furnaces. Their capacities are relatively small, say around 10 tons per day, but their efficiencies in respect to fuel consumption, degree of desulphurization, and richness of sulphurous

gas are high, and they have been well adapted to European conditions, whereas they were unsatisfactory when tried in the United States. However, some of the more recent plants of Germany were implemented with furnaces of the McDougall type.

Except for survivals of old construction, muffle furnaces have passed out of use in connection with blende roasting for sulphuric acid manufacture. The control of the gases from furnaces of the McDougall type is so good that they go directly to the Glover towers without need for dispersing separately the combustion gas from carbonaceous fuel.

With most of the modern roasting furnaces, coal consumption ranges from 20 to 10 per cent of the weight of the raw ore, varying according to the type of furnace and the quality of the coal. The best practice is nearer the lower figure than the higher. Instead of coal, natural gas or petroleum may be used. With petroleum as fuel, roasting may be done with 12 gal. per ton of ore, which would be equivalent to about 180 lb. of coal, or 9 per cent. For the purpose of enriching the gas in sulphur dioxide and increasing production of sulphuric acid, brimstone is sometimes burned as a booster and plays the part of a fuel. The brimstone may be burned in a kiln feeding its gas into the ore roaster, or it may be burned in the roaster itself.

Most of the several furnaces of the McDougall type differ only in details such as design of the rabbles and rabbling arms, their attachment to the central column, and the slope of the hearths. The Warner-Ingalls furnace is distinguished by having walls 18 in. thick, flat horizontal hearths, complete circulation of the cooling air through the rabbling arms, introduction of the cooling air at the top of the shaft and discharge of it at the bottom (which is the reverse of the ordinary), transfer of the hot air from the cooling arms through pipes into the four lower hearths, and feeding the ore through vertical drop pipes to a series of hearths in stages. Through these means for the conservation of heat, blende may be dead-roasted without the use of any extraneous fuel.

In all the modernized furnaces of the McDougall type, a great deal of the efficiency is realized from the burning of the ore as it showers from one hearth to the hearth next below. This idea was further developed at Trail, B.C., by taking out the hearths of the Wedge furnace between the uppermost and the bottom and letting the ore shower down. This is now described as shower roasting or flash roasting. It has the advantages of immensely increasing capacity, eliminating the costly maintenance of stirring mechanism, and otherwise reducing costs. These advantages are penalized by a large escape of dust from the furnace with the necessity for providing enlarged means for its collection and re-treatment.

At Avonmouth, in Great Britain, desulphurization is accomplished by making repeated passes of raw ore over a very large sintering machine.

In modern zinc metallurgical practice, blende roasting is done with the furnaces and adaptations of them already described. Many of the varieties of roasting furnaces formerly described are now obsolete, although survivals are still to be found in use in the older plants. The important thing is that blende roasting has been made autogenous, *i.e.*, the heat of desulphurization is caused to do the work, and even with realization of a surplus of heat that may be utilized otherwise.

The modern furnaces of the McDougall type are economical of labor and fuel, but require considerable cast iron and ferrochrome in the upkeep and replacement of their stirring arms and rabbles. In dead-roasting for subsequent zinc distillation, the use of iron and ferroalloy may be as much as 1 lb. per ton of ore roasted, about half as cast iron and half as ferrochrome. Operating labor may be 0.16 to 0.22 man-days and use of power, 13 to 15 kw.-hr. In roasting as a preliminary to electrolytic extraction, the temperature is lower and the requirements for iron are less. In a record of 100,000 tons of ore roasted, the use of cast iron per ton of ore was 0.33 lb.

and of ferrochrome only 0.026 lb. In shower roasting all these quotients are reduced at the expense of increased cost of dust collecting.

Sintering.—In the majority of plants treating sulphide concentrates, both in Europe and America, the ore is sintered preliminary to distilling. This is done for the sake of better desulphurization, which may be carried as low as 0.25 per cent sulphur, and for the sake of improved results in distilling, which follow principally from (1) the better desulphurization and (2) betterment of reduction. This improvement may have been of the order of 4 per cent; *i.e.*, recovery of zinc may be raised from 86 to 90 per cent with reference to the same ore and same practice. However, this is not to be interpreted as a broad generalization; for a plant that was already enjoying good roasting would naturally experience less improvement by virtue of sulphur elimination than a plant in which the roasting was not so good. In general, we had confirmation of the classic theory that one unit of sulphur holds back two units of zinc.

On the other hand, the introduction of sintering carried with it some penalties. It introduced another process, involving the use of heavy machinery requiring attention, power for driving, and upkeep. It introduced also a new outlet through which zinc might escape. However, the total loss of zinc in roasting plus sintering may be as low as 0.5 per cent. In general, it will probably be somewhat higher than that.

In sintering there are two major practices of general use, and two more that are of special use, *i.e.*, employed in single plants or by single operators. The major processes are the original Rigg method, in which the ore is preroasted down to about 9 to 10 per cent sulphur and is then sintered. In the United States this is used only at Bartlesville. The other process is the Baelen method, in which the ore is dead-roasted, or nearly so, and then is sintered with admixture of 4 to 6 per cent carbon.

In both these processes the gas that is drawn off from the wind boxes was originally so low in sulphur dioxide as to be useless for manufacture of sulphuric acid, and with the Rigg method there was consequently a considerable loss of sulphur. At Avonmouth, however, by the use a special seal (1928) covering the joint between the pallets and the wind boxes, dilution was reduced and gas of sufficiently good strength for sulphuric acid manufacture was obtained. This was improved elsewhere by making the pallets slide on a well-greased track, mechanically oiled.

The two special processes are those that are used at Avonmouth and at Overpelt. At Avonmouth, raw ore is desulphurized and sintered by repeated passes, to which reference has been made herein under Roasting.

In the Overpelt process the ore is preroasted down to 5 to 7 per cent sulphur and is then moistened with water to which a small proportion of ferrous sulphate is added. The mixture is kneaded and extruded as threads about 4 mm. in diameter and 20 mm. long. After drying, these threads are delivered to the sintering machine, which is able to take a bed about 20 in. deep—manifestly much more than can be charged with fine ore. The purpose of the Overpelt process is obviously to increase the porosity of the bed. The sintering is so expedited that the production of 213 lb. of sinter per square foot of useful grate area per hour is realized. Desulphurization is carried to less than 1 per cent total sulphur, and a gas containing 5 to 5.5 per cent sulphur dioxide is obtained and used for making acid.

In the United States the only sintering apparatus used is the Dwight-Lloyd straight-line machine, which functions like an endless belt, the pallets dumping at one end. In Europe the Dwight-Lloyd straight-line machine is used extensively, but there is also a considerable use of the Schlippenbach, an annular machine, in which the pallets move in a horizontal plane above a ring of wind boxes and trip for their discharge in a blank segment.

There are some differences in control of the operation. Some metallurgists prefer to produce a hard porous sinter, while others prefer a soft friable sinter. This means that in one instance the ore is more extensively fritted than in the other, and of course the nature of the gangue of the ore has a good deal to do with this. There are also differences in practice in respect to the degree of crushing the sintered cakes, the carefulness of sizing, the return of fines, etc. Reduction of cadmium, volatilization, and loss of it obviously occur. By the addition of salt to the charge, lead may be chloridized and volatilized, the ore being thus purified. Such modifications have been the subjects of patents. Reference may be made to the following chapter on Cadmium, page 469.

Dust Collecting.—In roasting with multiple-hearth furnaces of the McDougall type the escape of dust attains large proportions, and with flotation concentrates it may rise to 8 to 10 per cent of the weight of the raw ore charged. The dusty gas escaping from the furnace is commonly led through a brick chamber in which a good deal of the dust, perhaps 50 per cent, settles by gravity, and thence through a Cottrell precipitator designed for hot gas; for of course the clarified gas must reach the Glover tower at a temperature high enough for it to function properly for sulphuric acid manufacture.

In a few plants, dust collection is effected by means of improved Siroccos, which are highly efficient as dust collectors from cool gas but in the course of time operate with impaired efficiency on hot gas containing lead fume. Nevertheless, chamber acid has been made successfully with no other means of dust removal.

In roasting a blende containing cadmium and lead, a large part of the former and a considerable part of the latter are volatilized and recaptured in dust and fume. In roasting an ore containing 0.25 per cent cadmium, the cadmium may commonly be recaptured in the flue dust up to a tenor of 4 per cent, all of it as water-soluble sulphate. Lead is precipitated in the Cottrell fume as sulphate. These products may become sources of cadmium and lead, respectively, as by-products.

Conveying, Cooling, and Mixing.—The calcines discharged from the roasters are conveyed away mechanically by closed conveyers, good forms of which are the Jacoby, the well-known endless-screw, and the push-plate. The calcines may be discharged into a cooler, a long cylinder revolving in a tank of water, in which their temperature may be so reduced that they may be safely dumped into the bins or tanks from which the sintering plant is fed. Up to, and through, the sintering plant all operations are performed in enclosures within which dust is confined or from which escaping dust may be recaptured.

The calcined or sintered ore, crushed and screened, is mixed with the desired proportion of reducing carbon and perhaps the addition of about 1 per cent of sodium chloride. The function of the latter and the practice in respect of it will be discussed later. For reducing coal a good many materials are employed, largely according to availability and cost, *e.g.*, anthracite fines or duff, coke breeze, a mixture of coke breeze and slack coal. Major considerations are not to have too much volatile matter, the minimum of ash, and the minimum of sulphur. As a reducing agent there is some difference in the activity of certain carbons. Charcoal would theoretically be the best.

Reducing coal performs the double function of reducing zinc oxide and also acting as a sponge to hold up molten slags and so protect the retorts. In most American works, the amount of reducing coal used is now 30 per cent or less. It used to be as high as 45 per cent or more. In speaking of these percentages, we always mean the wet weight of the material rather than the dry weight of its carbon.

The mixing is done mechanically, in substantially the same way as the mixing of concrete. The same type of machine is employed for both. In American practice

the mixture is deposited in cars that are trammed to the furnaces, from which it is shoveled directly into the retorts. In some European practice the charge is deposited on the floor immediately in front of the furnace, and if blue powder and other between products are going to be mixed with it that is about the only way to proceed. With mechanical mixing the responsibility of the mix-room foreman is great, for thorough mixing is important. Even after that has been accomplished there is the possibility of resegregation in subsequent handling, considering that the mixture is composed of materials of quite different specific gravity.

Distilling.—In general practice all over the world distilling is performed in a cycle of 24 hr., of which the maneuver (the operations of drawing spent residue, scraping of condensers, recharging, replacing condensers, replacing broken retorts, etc.) occupies 5 to 2 hr., the latter being exceptionally low, and 4 hr. being about the lowest of good practice in general. After gas has been turned on, about 2 hr. is required for the performance of preliminary reactions, following which the condenser flames become purple and then begin to show tinges of green from burning zinc. The time of active distillation is therefore about 18 hr.; the first quarter is a waxing period and the last quarter is a waning period. Manifestly, the greater the celerity of performing the maneuver, the longer is the period of active distilling, but of course the temperature gradient is an important correlative factor in all this. The cycle might be prolonged from 24 hr. to 30, 32, 36, or 48, and improved recovery with less breakage of retorts may be obtained, but with some increase in costs and with ingenuity in the arrangement of human attention. All these cycles have been tried tentatively, especially in plants in Oklahoma, and at present at least two plants are operated on a 48-hr. cycle.

The smelteries of Oklahoma operating on a 48-hr. cycle have raised their percentage of zinc extraction from about 90 to about 94, computed on the basis of the zinc content of sintered ore entering into the charge for distilling. This improvement is accomplished at some increase in cost for labor and fuel, but not so much as to prevent a net gain from the operation. The improvement in zinc recovery is ascribable to better condensation, resulting from the slower and more regular delivery of zinc vapor from the retort, thus ameliorating the bad proportions between retorts and condensers that are inherent in the American type of Belgian furnace and also the absence of prolongs, the use of which our labor conditions do not permit. The cost of fuel per ton of ore increases only moderately, owing to the lower furnace temperature. Gas per ton of ore for 48 hr. is about 1.3 times what it is for 24. The cost of labor also increases only moderately, because in the intervals between the maneuvers (every other day), there is on duty only a metal drawer, and in firing with natural gas (as in Oklahoma) the labor of attending to furnace temperature is but slight. Finally, if a plant has a surplus of furnaces, its capacity is not diminished by using them in this way. Except under such special conditions, the 48-hr. cycle does not appear to commend itself.

Furnaces.—With but few exceptions the zinc-distilling furnaces of the world are now gas-fired and heat-recuperative in one way or another. Gas is derived from gazogenes, which are installed in batteries near the furnaces, or perhaps in a central plant from which it is piped to all furnaces. The gazogenes, or producers, themselves are of standard types, and as they are employed in great variety they need not be described here, nor even mentioned. Palmerton to a considerable extent employs gas from its spiegeleisen blast furnaces, and Rosita has used coke-oven gas, both of which come to the same thing as a central plant. In the American Southwest, natural gas is employed. Distilling furnaces have been fired with petroleum and with coal dust, but those have not been common practices and are of interest only as precedents.

Except for our American natural-gas-fired furnaces, almost all distilling furnaces are heat recuperative, indirectly if not directly. The Hegeler furnaces of the United States deliver their products of combustion through waste-heat boilers for generating the steam required in the plant, and the credit for that reduces the furnace quotient to a reasonable figure, perhaps as low as 1 ton of coal per ton of ore. The steam generation is usually short of the plant requirement for power and may have to be boosted by accessory coal-dust firing. Steam boilers may follow regenerative furnaces, but that is unusual and ought not to be necessary if the checkerworks are of adequate capacity, which is not always true. Of the truly recuperative furnaces, the continuous countercurrent system has surrendered to the alternating reversing, or Siemens, system.

Of the reversing regenerative furnaces there are several major types, but their number is not large in respect to differences of principle. In one major type there are four checkerworks, two for air and two for gas. In another major type there are only two checkerworks, which are only for preheating air, and the gas producers are then preferentially put close to their furnace so as to deliver the gas with as much as possible of its initial heat. On the basis of these fundamental differences, furnaces will be distinguished according to the movement of the gas currents within their combustion chambers.

The original Siemens furnace (known as the Auby furnace) has four checkerworks, and the gas and air issuing from their ports rise and descend alternately over a middle wall. Furnaces of this type are used at Rose Lake (Fairmont City) and Palmerton in the United States; at Stolberg (Birkengang works) and elsewhere in Europe; indeed, quite generally in Germany. The Welzer furnace has four checkerworks, from which the gas and air reverse in alternate directions. This furnace is used at Overpelt and Lommel, in Belgium, at Uethemannhuette in Upper Silesia, and elsewhere. The Tanier furnace that was developed at Sclaigneaux is a modification of the Welzer and is used extensively at other plants in Belgium and in the north of France. The Van Gulck furnace has checkerworks for preheating air only. The gas and air reverse over a middle wall, as in the Auby furnace. The Van Gulck furnace is used at Avonmouth and at Swansea and formerly at Mortagne.

The Dor-Delattre furnace, which was developed at Budel, also has checkerworks only for preheating air. It is distinguished from all other distilling furnaces. Instead of having the checkerworks in the inferior structure, the Dor-Delattre has them at the end of the superior structure and conveys the gas and air through longitudinal canals above the combustion chamber instead of beneath it. In the Berzelius works at Duisburg the furnaces are of similar design. Asturienne has Dor-Delattre furnaces at Auby and at Aviles (Spain), and when Vieille Montagne rebuilt Flône and Valentin Cocq it adopted this form of furnace. The Dor-Delattre design permits the checkerworks to be built of adequate capacity, only at the expense of floor space; whereas when they are built in the lower part of the furnace, they are subject to certain limitations and frequently are not made large enough. The Dor-Delattre system may have some other advantages.

Except the Dor-Delattre furnace, all the regenerative distilling furnaces have their checkerworks in their substructure. As to their superstructure it is now difficult to classify sharply between the Belgian and the Rhenish type, for whereas some furnaces exist in their purity, there are many that share the characteristics of both types. The Rhenish furnaces of Europe have commonly 216 to 288 retorts of 2 to 3 cu. ft. internal volume, arranged in three rows, the two fronts being divided into closets, each containing the condensers of two retorts. The Belgian furnace has retorts of smaller volume, say 1.5 to 2.2 cu. ft., and more of them; the Dor-Delattre has 432, arranged in six rows, but five-row furnaces are more common. In the United States

our Hegeler furnaces have commonly 608 retorts in four rows. The Neureuther-Siemens furnaces have commonly 800 retorts in five rows. In general, the tendency in the United States has been to reduce the number of rows to four, especially in the Hegeler and natural-gas-fired furnaces. American metallurgists generally stick to the cylindrical retort, but some have adopted retorts of elliptical cross section, and in certain instances their axes are as large as those of the Rhenish retort. In all American furnaces the inner ends of the retorts rest on ledges projecting from the middle wall. Such construction also obtains extensively in Europe, but with the pure Rhenish furnaces there is no middle wall, the arch springing from face to face, while the inner ends of the retorts rest on the ledges of a perforated wall or banquette, which with retorts of great length, up to 72 in., and even 78 in., when an intermediate support of the same nature is provided. In American practice, retorts longer than 54 in. are seldom to be observed, although we do go up to 60 in.

Even with the purely Belgian furnaces the *devanture* (the front structure) is deeper in Belgium than in America, *i.e.*, the condensers do not stick out so far beyond the plane of the face of the furnace. The Dor-Delattre furnace has a shield that can be pulled up or down, more or less like a Venetian blind, protecting the front of the furnace against drafts of air. The same thing was in the mind of E. C. Hegeler when he surrounded his entire furnace with a curtain of sheet iron, which also is to be seen at Danville. The Rhenish furnaces usually have hoods extending along each front of the furnace, connecting with a main, through which noxious gas and fume are drawn off. Escaping zinc oxide, chloride, etc., may be recovered from this system, but trials in the way of doing so have demonstrated that it is not worth while. The prolongs themselves are effective collectors. From a European zinc distillery there does not hang the great cloud of white smoke that hovers over many American plants.

The essential requirements of a distilling furnace are economy of fuel, uniformity of temperature, and such arrangement of inlets and outlets for gas, air, and combustion products that they do not become clogged with dripping slag, dust, etc. Economy of fuel results from the proper proportion of retort space to combustion chamber, and of checkerworks, together with avoidance of excess of secondary air. Uniformity of temperature is accomplished by the proper distribution of combustion and restriction of the alternating travel of the burning gas. In any reversing regenerative furnace, whether the currents are up and down, down and up, or end to end, there will be a neutral zone midway, where the furnace temperature will be slightly inferior. In the old Siemens furnace this zone will be above the middle wall, where there may be a fall of 50°C. in the furnace temperature. The metallurgist aims to achieve an even glow of white heat throughout the combustion chamber. In furnaces of the Welzer type (end-to-end reversal) the neutral zone is probably reduced to the minimum, for the gas and air enter alternately through ports almost up to the median transverse line.

Plant Layout.—Modern zinc-distilling furnaces are built entirely above ground, except for their foundations, and are attended from the upper floor. The residues drop into side pockets, from which they slide into cars to be trammed away. Sometimes a mechanical conveyer is provided for that purpose. American furnaces of the Hegeler type and those in the natural-gas fields still have ash tunnels under them through which residues are removed.

In European plants the furnaces are commonly lined up end to end with the retort-tempering ovens between them, several furnaces being grouped in a hall. Such a layout exists at Palmerton, but elsewhere in the United States the furnaces are laid out in parallel, each in its own house, except in the natural-gas fields, where there are two per house. In the vernacular of those districts, the separate furnaces are called "stoves," a pair of them still being regarded as a "block."

Most zinc-smelting plants having been evolutionary, there are to be observed in them unbalances among functional departments and irregularities in equipment, such as furnaces of different types, different sizes of the same type, and different forms and sizes of retorts in the same furnace. Sometimes metallurgists consider that they have good reasons for variations; *i.e.*, elliptical retorts in the lower three rows and cylindrical in the upper two may be held advantageous for certain furnaces and certain ores. The ideal plant has all functions in balance in multiples of two and all parts alike in each department. Thus, there may be four roasters, four acid systems, two sinterers, and eight distillers, with no bottlenecks among the several departments.

Retorts and Condensers.—The essential features of the process of distilling in the intermittent way are the retorts and condensers, which are made in a separate factory of the plant that in the American vernacular is called the "pottery." From this the retorts, after seasoning (drying), are delivered to the distilling furnaces day by day as required, and after tempering in a near-by kiln, where they are brought slowly up to the bright red heat, or as nearly to furnace temperature as possible, they are drawn out for making replacements in the furnace.

The batch for making retorts is a mixture of burnt clay (chamotte, grog) coarsely crushed and of raw fat clay in proportions of 50:50 to 60:40. The chamotte forms the skeleton of the concrete and the plastic raw clay is the binder. The more chamotte, the stronger is the retort; the more fine clay, the less porous is it. A physical balance has to be struck. There are also chemical considerations insofar as the character and composition of the clays, together with other materials, may be adjusted to the character of the gangue of the ore, from which slags will result. If the gangue is siliceous, the retort should also be strongly siliceous; if the gangue is basic, either from iron or lime or both, the retort should be aluminous or inert.

In accomplishing such purposes, substitutions for parts of the chamotte and clay are made. A common substitution almost everywhere in Europe is the introduction of coke dust, which should be as fine as possible, to the extent of 10 or 15 per cent, but in America this is scarcely ever used. The coke dust tends to give the retort somewhat of the qualities of a graphite crucible. Another substitution is the introduction of some granular quartz, for the purpose of making the retort more siliceous. However, inasmuch as quartz has a higher coefficient of expansion than clay, the grains of it tend to have a rupturing effect when the retort is heated. This is counteracted by adding the silica in the form of flour, which during recent years has been widely adopted in American practice. A mixture might be, for example, 25 per cent chamotte, 25 per cent silica flour, and 50 per cent clay. Such retorts have done very well with siliceous Joplin ore. Another innovation has been the use of carborundum retorts, *e.g.*, 65 per cent carborundum and 35 per cent clay, which has occurred both in Europe and America and has offered the theoretical advantages of better heat conductivity and long life. With the retort of unchanged diameter, other conditions remaining the same, the better conductivity may increase zinc recovery by 2 per cent; or the diameter of the retort may be increased (as at Amarillo and Rosita) and heavier charging may be accomplished with undiminished zinc recovery. The life of the retorts may be tripled. With ferruginous ores and furnaces fired with producer gas, however, ventures with carborundum retorts in some instances have been quite disastrous, the retorts suffering corrosion from the outside as well as from the inside. Naturally, the carborundum retorts are much more costly than the clay retorts. The carborundum retort is therefore a utensil of occasional rather than of general use.

With all types of retorts, it is obvious that the thinner the wall, the better the conductivity. Practice has everywhere for a long time settled on a wall thickness of about 1 in. and a butt thickness of about 2 in. As among the ordinary clay retorts,

the graphitized retort, and the silica-flour retort, there does not seem to be any material difference in conductivity as determined by pyrometric observations or in the way of zinc recovery apart from the matter of breakage.

In cross section and dimensions the retorts that are used at present are of wide variety. The commonest form of the Belgian retort is circular, 7½ to 8 in. in diameter. Extensively used also are retorts of elliptical cross section. While we so describe them, they are really two half-circles joined by a rectangle, which gives them straight sides. Dimensions may range from 6½ to 7½ in. for the short axis (width) and 9 to 12 in. for the long axis (height). As a general principle, reduction in width improves penetration of heat, reduces retention of zinc in the residue, and improves recovery. Height is not a factor in this. Reducing the width of a retort from 8½ to 8 in. brings about a striking improvement, from 8 to 7½ further improvement, but not so strong, from 7½ to 7 and from 7 to 6½ still further improvement, but at diminishing rates. In going below 7 in., there is increased difficulty in charging.

Besides the circular and elliptical cross section there are also the muffle-shaped (not much in use now) and the oblong (with rounded edges), the latter to be much commended. Different forms and dimensions may be produced by simply changing the die of the press.

In length, inside dimensions, retorts run generally from 48 to 72 in. In European practice they are longer than in American, for we seldom go beyond 54 in. The ability to charge well and mechanical strength are of course governing factors. We may consider the retort as a hollow beam, constructed of fragile material, supported at each end and carrying a uniformly distributed load of perhaps 250 lb. at temperature of perhaps 1500°C.

The cross section of the retort and its length compound into cubic measure, or internal volume or capacity. In use in the United States are retorts ranging from 1.5 cu. ft. (old) to 2.2 cu. ft. In Europe in some Rhenish furnaces they are of 3 cu. ft. In general there has been in recent years a tendency to increase volume for the sake of increased charging. Retorts 1.9 m., or 76 in., in length are on record.

In all modern plants the retorts are molded under a pressure of about 150 atm. by means of the Mehler or Dor-Delattre hydraulic presses, which are improvements of the original Dor press. The molded retorts are transferred to the drying rooms, where they season by gradual loss of their water. As freshly molded, they contain 12 to 15 per cent water and are introduced into the drying rooms at a temperature of 60 to 70°F. With a gradual rise in temperature after the first 15 days, their water content will have been reduced to about 2.5 per cent at the end of 30 days, to about 1 per cent at the end of 60 days, and to about 0.3 per cent at the end of 90 days, the temperature being gradually elevated to something like 130°F.

Practice varies in respect to the speed and duration of drying. Some metallurgists use their retorts after a month of drying, while others insist on 3 months, or 4 months, with a slow increase of temperature. There are records of substantial increases in retort life as a consequence of care and patience in this particular. At the best, a retort of clay or other refractory material is an imperfect vessel, being subject to porosity, to microscopic cracks, and to differences in strength when regarded as a beam. Retorts may be tested by closing them with an airtight cover, pumping air into them under pressure, as into an automobile tube, and painting the exterior with a solution of soap. Loss of pressure, which is always rapid, correlates with development of soap bubbles on the exterior, which are uniform if the retort is homogeneous, but irregular if there are microscopic rents, which let the air out very quickly. In order to counteract porosity, the retorts in European practice are commonly dressed inside and out with a slurry of powdered glass and soda, or similar composition which upon burning glazes the retort. Such glazing is seldom done in American practice.

In pugging the mixture of refractory materials and cutting it up into blocks for introduction into the press, care is taken to avoid trapping air or to allow for its escape before pressing. Otherwise, it may be entrained in the molded retort, and may even appear as blisters, impairing the quality of the retort. At Donora, the Wettengel pug mill has been modified by interpolating a vacuum chamber between the compression zone and the extrusion barrel and thus de-aerating. This has been found to increase the mechanical strength of the retort, increase its density, reduce drying time, and increase life in furnace, at an immaterial increase in costs for the power requirements for the vacuum pump.

Condensers are made from mixtures of clay as for retorts, but inferior grades are used, and old retorts, cleaned of slag and crushed, often take the place of chamotte. In the United States, most condensers are of the simple conical form and are made by a machine that forces a conical mandril into a conical mold containing the requisite quantity of clay. A belly may be produced in the tube by cutting out a gore from the larger end and drawing the two sides together, which, of course, is handwork. Condensers have been made by machine molding, with a diameter at the large end that is greater than the interior diameter of the retort to which it is to fit; it is reduced to fit by inverting the molded condenser into a conical ring, which is called "crimping." This produces a bottle-shaped condenser and may increase the interior area from 300 sq. in. to about 360. Many different shapes of condensers have been, and are now, used. The more complicated they become, the more handwork is required. The old Rhenish condenser was a substantially rectangular tube, rounded at the top. The Dagner condenser, used in Upper Silesia, is a composition of rectangular tubes.

In length the Belgian condensers vary from 18 to 24 in., while the Rhenish and Silesian condensers were about 36 in. long. Recently, some of the Belgian metallurgists have increased the length of their condensers, even to as much as 36 in. This subject is complicated and will best be discussed further on when furnace operation is considered.

Condensers are sometimes burned prior to use and sometimes are used unburned. Either way the breakage of them is large, and as will be seen subsequently, this is a very important matter. The breakage is partly mechanical, from careless handling, and partly chemical. The latter is evinced by splits occurring while the condenser is in place and not being handled, such as a longitudinal rent or a ring rent that may let the nose fall off. Specks of iron oxides in the clay and the action of hot carbon monoxide may have something to do with this.

Coal Consumption.—The records are generally not comparable, for they fail to take into account the value of the coal, the grade of the ore, and other variables, among which are both the type of furnace and the proportions of the furnace. The thermal efficiency of the best furnace is so low that large changes in the charging may be made without affecting the quantity of coal burned in the producers, but greatly altering the quotient of pounds of coal per ton of ore. The temperature of the products of combustion escaping from a regenerative furnace to the chimney is not even a true gauge, for though a temperature of 300°C. looks good the volume of the wasting gases may be too high, which it always will be if the excess of secondary air is too great.

Our practical deductions therefore are quite empirical. A Hegeler furnace distilling ore of 70 per cent grade with gas produced from coal of 13,000 B.t.u. may give a figure of 1½ ton per ton of ore, which with a steam credit of one-third may be reduced to 1 ton net. On the same grade of ore a regenerative furnace with coal of 12,000 B.t.u. may give a quotient of 1.1 ton, which perhaps might be reduced by heavier charging. With the best regenerative furnaces and the best practice, coal quotients of 0.9 and 0.8 are rather common. One furnace is known that with coal

of 13,000 B.t.u. used only 0.72 over a month. These figures are very different from those of the old direct-fired furnaces that used to consume 3 or 4 tons of coal per ton of ore. However, when we look at the New Jersey continuous furnace and see quotients like 0.5, we are conscious that we still have some distance to go. We should not overlook that in intermittent distilling there is a period of 6 hr. or so, including the time of the maneuver, when the furnace has to be kept hot without doing any directly useful work, whereof 0.8 ton in one case and 0.5 in the other are not perhaps very much out of harmony.[1] We may also be cognizant that the intermittent furnace, having to rework a large proportion of intermediate products, is required to do the same work twice over.

Reduction and Condensation.—The zinc oxide of some ores reduces more easily than that of other ores. One of the advantages of sintering has been improvement in that respect. The activity of the carbon employed as reducing agent also plays a role. Apart from such differences, the controlling factors in reduction are temperature and time, which are correlative. Time may be increased by shortening the maneuver or extending the cycle to something more than 24 hr. Temperature is limited by the durability of the retorts and the stability of the furnace. In European practice there are maximum temperatures of 1400 to 1500°C.; in American practice, 1300 to 1400°, but rarely as high as the latter. These are temperatures in the combustion chamber; inside a clay retort with a 1-in. wall the temperature will be 100 to 200° lower. The front ends of the retorts, resting on shelves, will not be so hot as further in, consequently there will be poorly reduced ore in that place. Carborundum retorts, because of their superior conductivity, run hotter toward the front than do clay retorts.

When the reduction of zinc begins and the vapor starts to come over, the preliminary reactions have not been fully completed and the gas is high in carbon dioxide, which as the temperature falls in the condenser acts oxidizingly on the droplets of zinc and produces blue powder, from which we are never entirely immune, although in the course of time the gas discharges with only about 1 per cent carbon dioxide. The blue powder, which to the naked eye is merely an impalpable dust, really is composed of microscopic globules, which show frostings and sproutings of zinc oxide that prevent the globules from coalescing. Amelioration of this is the rationale of the addition of about 1 per cent of sodium chloride to the ore. Volatilizing it is intended to dissolve the zinc oxide as chloride or oxychloride and so clean the pellicles of zinc and allow them to melt down. Probably that occurs. Anyway zinc chloride is found in the prolong dust. This spells a loss of zinc, though perhaps no more than will be suffered in redistilling a larger quantity of dust. At all events, the addition of sodium chloride to the ore is not essential and in some practice has been abandoned. In the absence of salt, the condenser flame is of course deprived of the sodium coloration, which is a guide to old-time furnacemen.

The observation may be made that in American practice it is common to "stuff" the condensers, *i.e.*, partly to close their outlet, allowing the gas to escape through a small hole, which is kept open by constant "spiessing." This gives a certain internal pressure in the retort and condenser, and if this becomes too much, through inattention, the gas and vapor may break out through the luting around the joint between condenser and retort. When prolongs are used on the condensers, they are open. If the prolong is on tightly, the gas escapes through only the small hole near its end.

A logical condenser is a long pipe folded in zigzag and enclosed in a closet whose temperature can be controlled, as in the Dagner condenser of the Silesian furnace, but this is not easily applicable to a furnace of more than one row of retorts or to the

[1] In using this illustrative quotient for the continuous furnace, I have in mind data prior to utilization of the gas escaping from the condenser.

practice of daily taking down and putting up. The Belgian and Rhenish furnaces with condensers registering with the retorts are restricted in length by thermal conditions, which is not, perhaps, of great importance inasmuch as lengthening may not add much to internal superficial area; and increase in girth is restricted by lack of room and difficulty in getting at the joint for luting, etc.

As the internal volume of the retort is increased and the density of charging is also increased, there should be a corresponding increase in the capacity of the condensers. With a retort of 1.75 cu. ft., the condenser may have 300 sq. in. of internal surface. With a retort of 2 cu. ft. the internal area of the condenser may be 400 sq. in. The latter is about a practicable limit. These are only rough guides. The correlation between volume of retort and condenser surface is naturally affected by the quantity of zinc that is charged into the retort and the evenness in distilling it.

Charging.—The practice of keeping up the condensers and charging through them by spoon prevailed extensively in Europe until recently, but most works have gone over to the Belgian practices of making a condenser that fits the retort, taking it down and putting it up every day and filling the retort by throwing in the charge.

The charger has one of the very responsible positions. His work is arduous. The idea of substituting mechanical charging for hand charging has consequently been engaging. Numerous mechanical chargers have been designed and applied on a regular working scale. These may be generalized as slingers and shooters, the former being designed to throw in the charge and the latter to shoot it in.

In general, the conclusion has been that with mechanical chargers there is no material gain either in labor saving or in efficiency of performance, and that when first cost, upkeep, etc., are considered, they are not worth while. At Rothem (in Belgium), however, the Dor-Delattre charger, which shoots in the charge, continued in regular use for a good many years. It put 13,000 lb. of ore into 210 retorts in 20 min., and reduced the total time of the maneuver to 2 hr., leaving 22 hr. for distilling.

Density of Charging.—Much attention has been given to increasing the density of the charge, which means increasing the number of pounds of ore introduced per cubic foot of retort volume. Accomplishment of improvement in this direction depends on several factors, among which are (1) the specific gravity of the ore; (2) proportion of reduction material mixed with the ore, for obviously the less reduction material, the more room there will be for the ore; (3) care with which the charge is thrown in, avoiding cavities; and (4) force with which the charge is thrown in. An expert charger can throw a shovelful of charge into the retort with such force as to break its butt. A mechanical charger can put a quantity of ore into a given retort that in comparison with the best hand-charging is almost unbelievable, and can do it so densely that a strong man is unable to drive in the spiess rod. Such excessive density of charging may introduce more zinc into the retort than, after reduction and vaporizing, the condensers are able to handle; therefore recovery of zinc may be impaired rather than improved. Up to this critical point, however, increase in density of charging is beneficial from the standpoint of metallurgical reactions in the same way that a briquetted charge may be beneficial.

In American practice, charging sintered ore weighing about 105 lb. per cu. ft., mixed with 30 per cent of reduction coal, wet weight, about 55 lb. of ore per cu. ft., or 110 lb. in a retort of 2 cu. ft. capacity, is charged; here and there that figure is exceeded.

Furnace Charging.—Although density of charging per retort has a good deal to do with the charging of the furnace as a whole, the subjects are two different things, although this is commonly overlooked, and the two expressions are commonly confused. The zinc that is reduced and vaporized is not wholly condensed directly as spelter. We may get 65 to 70 per cent of it as direct spelter, the remainder as zinc

dust, blue powder, which must be redistilled. Besides the blue powder that is skimmed from the ladles and recovered from the prolongs, there are other between products that must be redistilled, including the imperfectly distilled ore remaining in the front end, perhaps 10 per cent, of the retort, which in American vernacular is called the "sample" and in the Belgian vernacular is called the *gueules*, or "throats"; the cleanings from the condensers; and the cleanings from the pans on the floor along the front of the furnace. In good practice these collections may aggregate 20 per cent of the weight of the original charge; in careless practice they may run to 30 per cent.

In American practice this entire collection is described as blue powder. With the Hegeler furnaces it is recharged into the sections of retorts at the chimney end of the furnace. With the Siemens furnace it is charged into the uppermost row of the retorts. In Europe it is more generally mixed with the ore. In occasional practice it is reserved and redistilled in a separate furnace. Whatever the method, it occupies furnace room, increases the fuel and labor quotients per ton of ore, and subjects a certain portion of the zinc to a renewed opportunity for loss.

Translated into terms of furnace charging, if a furnace of 600 retorts, or 1200 cu. ft., should be charged fully at the rate of 55 lb. per cu. ft., it would receive 72,000 lb., but if only 480 retorts can be charged with ore the total is 52,800, and if only 420 can be charged with ore the total is 46,200, and all the quotients are altered accordingly. The furnace charging is therefore a composite of the density of charging and the proportion of between products.

These illustrative computations are exclusive of old condensers, which may be crushed and added to the charge or may be crushed and jigged and the concentrate added to the charge; or the concentrate may be accumulated and be distilled separately. All these practices are to be observed.

Losses in Distilling.—In present good practice, distilling sintered ore, the recovery of zinc is 90 per cent plus, exclusive of recovery that may be realized by the use of prolongs and of additional recovery by re-treatment of residues in one or more ways. Equally good recovery is accomplished from ore with irony gangue, or limey, or simple quartz if suitable adjustments are made by the metallurgist.

In considering the subject of zinc recovery, it is important to examine the ways in which loss of zinc occurs in distilling. Most important is its retention in the residue. Apart from that, the losses are scattered: absorption by retorts, retention by condensers, escape from condensers (if prolongs are not used), filtration through retorts and leakage by retorts breaking, contributing to loss up the chimney (which is a loss that is very difficult to measure). There is some recovery of zinc from dust and fume depositing in checkerworks and settling on furnace tops, but both are troublesome.

The loss is aggravated by the exigency of redistilling some between products. For example, we might expect to obtain 70 per cent of the zinc of the ore as spelter and 22.5 per cent as between products divided approximately as follows: in ladle skimmings, 16 per cent; in condenser cleanings, 2.5 per cent; in pan cleanings, 1.5 per cent; in "sample" (or throats), 2.5 per cent; all these being aggregated as "blue powder." Upon redistilling we may get from them 20 per cent (with reference to the ore charge), and the zinc recovery will be 70 per cent + 20 per cent = 90 per cent. The ultimate loss of 10 per cent may then be reckoned approximately as shown in the table on page 458.

The residue may amount to 30 per cent of the ore charged and assay 13 to 14 per cent zinc. Nearly half of its zinc content may be in oxidized form capable of being reduced. Daily loss of condensers was 15 per cent. Each discarded condenser contained about 7 lb. of zinc. By crushing and jigging, about two-thirds of its zinc could be recovered in a concentrate assaying about 70 per cent zinc, of course at a

certain cost. This salvage is not included in the analysis of recovery and loss. The absorption of zinc in retorts is computed on a basis of daily loss of 3.33 per cent (correlating with 30-day life). Each discarded retort carries away about 6 lb. of zinc. The loss of zinc escaping through the chimney is computable only by difference. It is more or less proportionate to the percentage of breaking retorts.

Direct spelter	70.0	
Blue-powder spelter	20.0	
Total spelter	90.0	
Zinc in ore residue	3.8	5.
Zinc in blue-powder residue	1.2	
Zinc retained by condensers	2.3	
Zinc absorbed in retorts	0.5	
Zinc escaping from condensers	0.5	
Zinc escaping through chimney	1.8	
Total accounting	100.0	

Many zinc-distilling balance sheets will be more or less in harmony with this. With the use of prolongs, the loss of zinc by escape from the condensers is practically excised. The loss of zinc by absorption in the retort is negligible. Old condensers generally assay about 30 per cent zinc, and the greater the breakage rate, the more do they carry away. Although the larger part of such zinc may be regained, there is additional cost, both for milling and distilling.

With regenerative furnaces there is some recovery of zinc from the checkerworks when they are cleaned. In one plant this averaged 25 per cent zinc by assay and figured to 0.3 per cent of the zinc in the ore charged. Cleaning of the tops of the furnaces also gives a product assaying about 25 per cent zinc and accounting for 0.2 per cent. This dust is used in the mixtures for stuffing and luting condensers, and so finds its way back into the blue powder.

The primary recovery of 92.5 per cent of the zinc that will be reduced to an ultimate recovery of 90 per cent, as already outlined, suggests that something better may be done with the blue powder than redistilling it in the primary furnace, whereof 20 to 30 per cent of its cubic feet of internal volume is occupied for this purpose. This is emphasized if, as in some European practice just prior to the war, the size of the retorts and the density of charging are increased so that no practicable condenser can be attached for the maximum collection of zinc and the only expedient is to increase the collection of zinc as dust in the prolongs. Such collection may exceed ability to market zinc dust. A rational expedient is then to apply the Thede process of rubbing the zinc dust in a heated revolving cylinder so that the cleaned zinc will melt down, this being similar to the Cornelius process used in Sweden (see the sections on Zinc Dust and Electrothermic Smelting at Trollhättan). This illustrates moreover the wide diversity of the factors in intermittent zinc distilling that must be considered and correlated in harmonizing any works practice.

According to Dr. Thede, describing the practice at Müensterbusch, Stolberg, Germany, where his process was introduced, the separate treatment of zinc dust costs only one-tenth as much per pound of spelter produced as redistilling, and with a smaller loss of zinc, so that recovery of zinc on the basis of the content of ore originally charged is raised to 95 per cent. The loss of zinc in the Thede process itself is small and chiefly mechanical. Moreover, by keeping the dust spelter separate the cadmium content of the direct spelter is reduced.

Metal Drawing.—Spelter was drawn from the Silesian and the original Rhenish condensers only once during 24 hr. With the smaller Belgian condensers, more draws

were necessary, and even more as the grade of the ore increased. In American practice, four draws are the common daily routine.

In quantity the draws vary according to the period, correlating with the activity of the distilling. The following is more or less typical of the draws in American practice:

Draw	From calcines, per cent	From sinter, per cent	Time
First	23	22.2	2.30 P.M.
Second	29	29.4	7.00 P.M.
Third	29.6	29.0	12.30 A.M.
Fourth	18.4	19.4	6.30 A.M.
Total	100.0	100.0	

This introduces the subject of the temperature gradient, or what may be plotted as the furnace thermograph. This is more or less variable according to the operating conditions. Beginning at 1000 to 1050°C. with "gas on" and immediately after completion of the maneuver, it may rise in a straight line, or in a slightly arched line, with different speeds. With a rapid rise the maximum, 1330°C., may be attained at 11.30 P.M. With a slow rise it may not be attained until 2.30 A.M. The rate of reduction naturally correlates with the thermograph. After the maximum has been attained, it is held level for several hours, or until the distilling of zinc is distinctly on the wane, nearing its end, when the temperature is allowed to fall to save retorts from being "butchered" when there is no longer an endothermic reaction occurring within them.

The temperatures suggested here are as registered by Seger cones inside an open retort. It is common practice to record furnace temperatures in that way, and temperatures in the combustion chamber by means of recording pyrometers. Even when the latter are used, however, the Seger cones afford a valuable check.

In European practice the spelter is commonly drawn into small ladles by hand. With some furnaces, the lowest row of retorts is so near the floor that nothing else can be used. In American practice a large kettle carried on a car on the rails in front of the furnace is universally employed. The spelter is drawn directly into this. When the kettle is full, the metal is skimmed and then poured into a row of molds. There is no question as to the superiority of this method.

Retort Residue.—After distilling has been completed, the spent residues must be withdrawn, usually by hand, but machines have been found useful in some plants, without becoming of general application. In some American practice a water pipe is introduced into the retort, letting out a little water, which immediately becomes converted to steam and blows out most of the residues. With the fluffy residues from Joplin ore this system works very well, but with a slaggy or "gummy" residue, it has to be hoed out.

Some lead from a leady ore goes over into the spelter. A considerable proportion of it may be recovered by gravity refining, but that which is retained by the spelter adds to the weight of the latter and realizes the spelter price for good ordinary brands. Most of the lead and all the gold, silver, and copper remain in the residue. If the silver content is high, which has occurred with some ores, the entire residue may be passed on to the lead smelter. In general, however, the residue used to be jigged for separation of its lead, together with the silver carried by it, if that were worth while.

The flotation process has been so effective in deleading ores that there is now but little need for recovery of lead from retort residues, but they are sometimes jigged and washed for recovery of undistilled zinc, unburned coal, etc. It is now a common practice to put retort residues through the Waelz process, burn out unreduced zinc, recover it as fume, and put that back into the charge for distilling.

Labor.—In the management of the zinc-distilling furnace there are two systems: in the one commonly practiced in America, the furnace crew of 30 or so is divided into groups of specialists, each group performing a single operation; in the other, which is in general practice in Europe, the furnace crew, which is always relatively small, is divided into squads, each of which takes charge of the operation of a part of a furnace, a half or a quarter, collectively performing all the operations of the maneuver. After the maneuver has been finished, the furnace passes into the charge of the fireman and the metal drawers, who work in the same way by either system.

An American furnace of 608 retorts was charged with 24 tons (of 2000 lb.) of ore and was attended by a crew of 30 men, inclusive of gas producers but exclusive of those who removed residues from the ash pockets. This figured to 1.25 man-days per ton of ore. Contemporaneously one of the most modern of the gas-fired furnaces in Belgium received a charge of 11 short tons of ore and had a crew of 20 men, which figured to 1.8 man-days per ton of ore. However, the Belgian furnace was operated with prolongs, which the American was not.

These labor quotients are computed on the basis of roasted ore. On the basis of raw ore in a well-mechanicalized plant in the United States, with furnaces fired with producer gas, the use of labor will hover around 2 man-days per ton of ore.

Refining.—Cadmium and lead both go over with zinc. Cadmium concentrates in the first draw of spelter. Lead is higher in the later draws. Some grading is accomplished by keeping them separate. Drawing into the large kettles in American use, there is some equalization of the molten metal, but even so there may be wide variations in the draws from different parts of the furnace, especially from our Hegeler furnaces that have so pronounced a drop in temperatures.

By remelting the spelter it can be equalized, and the excess of lead settles out. This is the simple process of gravity refining. Refining may also be done by redistilling, but that does not get rid of cadmium. The New Jersey process of reflux refining enables ordinary spelter to be raised to four-nine grade and in this respect puts the old process of intermittent distilling on equal terms with electrolytic refining.

The New Jersey Zinc Co.'s process of refining is a means of integrating in one operation multiple stages of fractional distillation and fractional condensation. The liquid metal and metallic vapor travel countercurrently through a column, the heat for boiling being supplied at the lower end of the column and the heat of condensation removed at the upper end. In practical application, spelter is melted in a pot whence it is introduced into what is called the "lead column," which comprises a series of superimposed trays of refractory material with staggered openings, permitting the liquid metal to cascade downward in intimate contact with metallic vapors ascending countercurrently. From the top of this rectifying column, zinc vapor passes into a condenser whence molten zinc issues into what is called the "cadmium column." From the top of the latter, cadmium is condensed as a dust or otherwise as a cadmium-zinc alloy. From the bottom of the cadmium column, refined zinc is obtained. From the bottom of the lead column, the metal from which the zinc has been mostly boiled off is collected in a liquating pot which gives impure zinc to be recycled and lead and zinc-iron dross separated by gravity.

The columns and their fittings are equipped from suitable refractory material. A refining unit is of 15 tons daily capacity, operating continuously. Prime Western spelter in this country, or g.o.b. metal in Europe, is raised to 99.99+ per cent zinc.

The direct production of this grade is about 96 per cent of the zinc in the feed; of the remaining 4 per cent all but 0.5 to 0.75 per cent is accounted for in the skimmings, dross, and other by-products. In connection with the New Jersey process of continuous distilling, the feed metal is run directly to the refining unit.

The New Jersey refining process is strongly patented and is used in the United States and in a few countries in Europe under licenses.

Zinc Dust.—In the United States there was a prewar production and consumption of about 15,000 tons of zinc dust, also called zinc gray and blue powder, and in Europe a larger quantity. In Europe where prolongs are used in the distilling of ore, the dust from them may be made commercial, and of a quality of 90 per cent zinc unoxidized, by sifting and grading. In general it is difficult otherwise to obtain such a grade directly from ore.

In the United States the prewar specification for prime zinc dust was 96 per cent metallic zinc, all to pass a 300-mesh sieve, together with some requirements as to grading according to size of particles. Close grading of size is more important than excessive fineness.

Spelter was formerly obtained from galvanizers' dross and other metallic zinky material by distilling in large bottle-shaped graphite retorts, commonly about 36 in. long and 20 in. in diameter. Furnaces with a battery of such retorts, commonly oil-fired, are still in use. Distillation of a charge requires about 18 hr. and a use of about 2 lb. of coal (or its equivalent of oil) per pound of dross and the labor of one man per shift per four retorts.

Some spelter is still produced in this way, but the quantity is greatly reduced and these furnaces are now used chiefly for the production of zinc dust, as being more profitable.

The treatment of galvanizers' dross and other zinc junk offers no very troublesome metallurgical problem, the zinc being simply boiled off and the vapor condensed either as spelter or as dust, the latter being accomplished by sudden chilling to a temperature of 320 to 415°C., which precipitates the zinc as snow, so to speak, instead of as rain. For this purpose a cast-iron canister may be used, and one 2 ft. in diameter by 4 ft. in height may collect 260 lb. of zinc dust in 24 hr. Either for spelter or for dust a commercial recovery of 80 per cent is about what is realized from galvanizers' dross. The loss is chiefly by retention in the residue of iron and lead that accumulates in the bottom of the retort until it is pulled out and broken up. There is a similar retention of zinc in connection with the cupriferous residue that accumulates in the distilling of zinc from old die-casting junk.

The zinc dust that is used by the electrolytic zinc producers is manufactured by atomizing molten spelter with a blast of air. There is a small production as a by-product from hot-dip galvanizing plants. In the modern technique of pipe galvanizing, and especially that of electrical-conduit galvanizing, the present practice is to blow through the pipes and tubes with dry steam under very high pressure. This gives a very fine dust, averaging upward of 95 per cent zinc as metal, that is collected by suitable means.

Zinc Burning or Zinc Fuming.—This is a process of reducing zinc oxide, which is distilled as vapor that is burned immediately. Theoretically, the metallurgical reactions are unchanged, but whereas in the recovery of zinc as spelter it is aimed to avoid oxidation of the vapor, the purpose is now to promote it, and to collect the oxide floating in the gas of combustion by filtering it through cotton bags. This introduces problems of cooling the products of combustion and dealing with them otherwise.

With ore free from lead and cadmium, and allowing coal ash, etc., to settle in the flue leading to the baghouse, oxide assaying 80 per cent zinc (the theoretical) and snow

white may be collected. The particles under a microscope will be in fractions of a micron ($\frac{1}{1000}$ mm. in diameter). The details of temperature, condensation, etc., that may cause these particles to be acicular, or of more equal dimensions or otherwise, will not be discussed here, nor the merit or demerit of different forms.

If the ore contains cadmium, it will go over into the fume, and will give it a color ranging from slightly yellow to distinctly brown. A slight yellowish tinge may be discharged, however, and it is possible to make a good grade of oxide from ore containing 0.3 to 0.4 per cent cadmium.

If the ore contains lead, it will surely be volatilized and filtered out with the fume as sulphate or some more complex oxidized form. The fume will no longer be capable of classification as "lead free," but will still be a valuable commercial product.

If the ore contains a good deal of lead, the product will be what is called a "leaded zinc," which is so valuable as a pigment that to some extent pig lead is melted and volatilized to boost a product derived directly from ore.

Zinc oxide of the highest grade is made by burning spelter; this is known as the French process and the product, French oxide. Zinc oxide as a finished commercial product is obtained directly from ore by means of the Wetherill furnace. Impure zinc oxide has been produced as a concentrate by the Pape process, by the Bartlett process, and by reducing in a reverberatory furnace, but those processes are now but little used, if at all. Recovery of zinc oxide from the blast furnace smelting brass junk is an important process practiced at Carteret and Perth Amboy, N.J., and Laurel Hill, L.I.

The present summary will treat only of the Wetherill process, the Waelz process, and slag fuming.

The fume collected from metallurgical by-products or waste products appears to run everywhere about 65 to 70 per cent zinc, the remainder being chiefly lead. This filtered fume is not an ideal product for re-treatment. It is fluffy, of low weight per cubic foot, and difficult to handle mechanically, either for shipment or for subsequent treatment. It may have to be densified by mechanical compression or by nodulizing by furnacing and may have to be deleaded.

Beneficiation of this fume may occur in the following ways, all of which exist in present American practice:

1. Return to the process of electrolytic extraction.
2. Delivery to manufacturers of lithopone (a hydrometallurgical process).
3. Delivery to manufacturers of lead-zinc pigment.
4. Delivery to zinc distillers. (With them it is not a warmly welcomed product unless it has been deleaded and nodulized. Without nodulizing it may, however, be mixed with roasted ore prior to sintering.)

Wetherill Process.—A distinguishing feature of the Wetherill furnace is the grate, which consists of a series of cast-iron plates, about 6 in. wide, 1 to 1.5 in. thick, and of length corresponding with the width of the furnace, which may be about 6 ft., these plates being perforated by conical holes about 0.25 to 0.4 in. in diameter on the upper side of the plate as it is to lie in the furnace and 1 in. in diameter on the lower side, there generally being about 100 holes per square foot. The purpose is to prevent a bed of ore and coal on the surface from sifting through very much and to prevent the holes from blinding. In some practice, the bars are perforated with narrow slots instead of conical holes. The bars rest on ledges in the side walls of the furnace. The ash pit is designed for operation of the furnace with an undergrate blast.

Furthermore, the two types of Wetherill furnace known as the Eastern and the Western differ only in details of design. The Eastern Wetherill is used at Palmerton, Pa. The Western Wetherill is used in the plants west of the Alleghenies. Exceptions to this generalization may be found in instances where furnaces of the Eastern

type have been built and operated more or less experimentally in Western plants. At Palmerton the ore that is treated is the franklinite concentrate from New Jersey. The Western plants treat ore from Tennessee, the Tri-State district, and from the region west of the Rocky Mountains.

The Eastern Wetherill consists of four or more hearths built together with a common back wall and with common side walls. The products of combustion from each hearth escape through an opening in its arch and are led to a chamber where the zinc vapor is completely oxidized, thence passing through a cooler to the baghouse.

The Western Wetherill comprises a series of hearths, separated only by low side walls and covered by an arch that is common to all the hearths comprising a block, the products of combustion being conveyed away from the end of the block.

In one plant where there were furnaces of both the Eastern and Western type, operated under identical conditions, no material difference in results was observed.

A Western Wetherill furnace of good design may have 10 hearths, each 6 × 12 ft., and may burn 24 to 25 tons of calcined ore per day mixed with 1.2 tons of coal, charging being done twice per day, and extraction of zinc from an ore of 70 per cent grade being about 87.5 per cent. Air pressure under the grate is equal to 2.5 to 4 in. of water. Length of furnace campaign may be 3 years.

Among plants, practice varies in operating details. The ore may be mixed with all the coal and so spread upon the hearth, or a bed of coal may first be laid and the mixture of ore and reduction coal then be spread on it. Three charges may be burned per 24 hr., or even four. The number of furnaces to a block may be 8, 10, or 12. The hearths may be as wide as 13 ft., *i.e.*, crosswise of the block. There are working doors on each side of the block, and the furnace personnel attends to one hearth after another. Mechanical charging has been satisfactorily applied, in which application all the coal is mixed with the ore.

With the Wetherill furnace it is necessary to counteract the tendency of the blast to break through the charge, making blowholes and craters. This requires constant attention. It prevented the mechanicalizing of the Wetherill furnace after the fashion of the traveling grate in steam-boiler practice, owing to the tendency of the air under pressure to break through along the sides and to slag and stick there. A great step in advance occurred when the New Jersey Zinc Co. began to make up the charge out of a briquetted mixture of ore and coal. The charge could then be burned like anthracite coal on a domestic grate, and the working doors of the furnace had no longer to be sealed. Obviously this opened the way to the mechanical Wetherill process.

In the operation of the mechanical Wetherill furnaces the charge of ore, plus about 20 per cent of coal, plus waste sulphite liquor from paper mills as binder, is compressed into hard briquettes, their shape being like that of a small pillow 2 in. square and about 1.5 in. through the thickest part. The grate bars of cast iron, which travel over sprockets at each end of the furnace, are 12 ft. long, which is the same as the width of the Western Wetherill furnace.

In operation the grate passes under a feed hopper from which it gets a bed of coal briquettes (of the same size as the ore briquettes), which are spread mechanically to a depth of 6 to 6.5 in. The coal briquettes pass through an ignition zone after which the grate receives from an overhead hopper a bed of ore briquettes about 6 in. thick. Reduction of zinc oxide and removal of the products of combustion then proceed according to the same principles as in the hand-operated furnace. Sticking of the charge to the side walls of the furnace is prevented by making them of water-cooled plates.

The mechanical Wetherill does away with the onerous labor conditions of the hand-operated furnaces, affords a much greater capacity per square foot of grate

surface, and by virtue of the intimacy of the mixture of briquetted ore and reduction coal gives an improved percentage of zinc extraction.

The Waelz Process.—This is a process of zinc reduction and burning by means of a revolving cylinder, internally heated to a high temperature, the mechanicalization being similar to the cylindrical furnace used for making cement. The Waelz furnace is built in sizes from 40 ft. in length and 6 ft. in diameter up to 160 ft. in length and 12 ft. in diameter. The slope downward from inlet to outlet is usually about 3 per cent. The rotation is generally about one turn in 55 sec., but it may be speeded to one in 30 sec. or retarded to one in 120 sec. For the largest furnace the power requirement is 25 to 30 hp., and the labor ranges from two to six men per shift. Ore and coke are mixed before charging. In the treatment of some low-grade calamine, the addition of coke has been as low as 10 per cent. In the treatment of retort residues, there may be sufficient unburned coke to allow the charge into the Waelz furnace to be self-burning.

In a plant in Upper Silesia, burning calamine with 12 to 15 per cent zinc, mixed with 25 per cent of reducing coal, 5 to 10 per cent of firing coal was used, and a zinc extraction of 95 per cent and a fume assaying about 66 per cent zinc and 6 per cent lead were obtained. About 160 tons of ore per furnace per 24 hr. was run. In the United States at the present time the Waelz furnace is used extensively in burning zinc out of current and old accumulations of distillation residues. A plant treating 300 tons of residues daily may yield 40 tons of fume or roughly 30 tons of zinc in fume. The yield is of course always commensurate with the quantity of zinc in the material that is treated.

It has been remarked before that even in good distilling in retorts about half the zinc in the residues is in oxidized form, perhaps partially as ferrate and silicate. Under the fierce internal heat of the Waelz furnace, further reduction is accomplished, and even a considerable proportion of zinc sulphide may be decomposed, reduced to zinc vapor, and burned. In this, as in other zinc-burning processes, the heat that is required endothermically for reduction is of course restored exothermically by combustion of the vapor.

If the Waelz fume is derived from leady ore, the fume itself will be leady. The fume derived from retort residues, however, will be low in lead inasmuch as such residues have been derived from ore previously deleaded. Such fume may therefore be returned to the ordinary process of distilling. This is done by mixing it with roasted ore prior to sintering.

Slag Fuming.—The treatment of slags from lead-smelting blast furnaces for extraction of their zinc content and recovery as oxidized fume is done on a large scale at East Helena, Mont., Tooele, Utah, Trail, B.C., and Kellogg, Idaho. The Bunker Hill plant at Kellogg, as the latest construction, sufficiently exemplifies the methods at the others.

Hot slag from the primary furnaces is transferred to the slag fumers. Some cold slag may be added. The slag-fuming furnace is 15 ft. long by 8 ft. wide and of standard water-jacket construction. On each side there are 14 double-inlet tuyères, each side being fed with a Babcock & Wilcox pulverizer of 4080 lb. of coal per hour rated capacity. They are designed to feed coal against internal pressure up to 10 lb. per sq. in. The pulverized coal (upward of 80 per cent through 200 mesh) is delivered to the tuyères in a primary air stream comprising about 48 per cent of the total air flow. The remaining 52 per cent enters the tuyères as secondary air. Two Ingersoll-Rand turboblowers, maximum rating 6910 cu. ft. each at 8 lb. gauge, supply the furnace air.

The coal-air mixture forced through the slag both supplies heat and effects the reduction of zinc oxide. The slag is treated in batches, each batch comprising a

furnace cycle, divided into three periods, *viz.*, charging, reducing, and tapping. Coal and air are delivered to the tuyères continuously throughout the operation, and the reduction period is about 65 per cent of the time of the cycle.

The dust-laden gas leaves the furnace at somewhat over 1100°C., enters the waste-heat boilers at 925 to 1040°C., and finally enters the baghouse at 200°F. The slag is dezinked down to about 1 per cent Zn. The fume assays 63 per cent zinc and 10 per cent lead and weighs approximately 40 lb. per cu. ft. It is densified and deleaded by mixing with about 1.5 per cent by weight of minus-¼-in. crushed coke and is calcined by passing it through a revolving cylinder, 75 ft. long by 7 ft. diameter, fired by either oil or coal dust, the temperature being about 500°C., at the feed end and about 1260°C. at the discharge end. Passage through this kiln nodulizes the raw fume, increases its weight to about 185 lb. per cu. ft., raises the zinc content to about 72 per cent, and reduces the lead to about 1.5 per cent. Fume from this kiln is delivered to a baghouse, whence a product with about 50 per cent lead and 23 per cent zinc is returned to the lead-smelting system via the Dwight-Lloyd sinterers.

The Bunker Hill plant was designed in 1943 for the treatment of 300 to 400 tons of hot slag per day. The operating personnel comprises 14 men per 8-hr. shift.

The production of zinc from the slags of lead smelting has now become an important process in the United States and in Canada. It gets the zinc from what are classed as lead ores and thus increases the extraction from an original zinc-lead sulphide ore by a substantial quantity. Moreover, it brings accumulations of old slag into the classification of new zinc deposits. In 1944, the three major plants in the United States treated about 510,000 tons of slag, which yielded 78,500 tons of oxide fume, containing about 55,000 tons of zinc. The cost per ton of slag is relatively low, but obviously it is substantially more for cold slag than for molten, and of course it is increased if nodulizing and deleading has to be done.

Continuous Distilling.—Obstacles in the way of designing a furnace for continuous reduction and distilling of zinc have been (1) difficulty of integrating in one operation the two stages of intermittent distilling, *viz.* (*a*) preliminary reductions and (*b*) the reduction of zinc oxide itself; (2) trouble from the ore becoming sticky and so hanging in a vertical shaft through which it was expected to descend; (3) inability of zinc vapor to find egress through a long column of fine ore, which cannot be "spiessed" as in the ordinary horizontal retort. Following many failures to accomplish continuous distilling, four processes have come into commercial use, although not all of them are in use at the present time. These are summarized in the following sections.

Trollhattan Process.—Some intelligent work was done in experimental plants to subject calcined ore to prereduction and then transfer it to an electric furnace heated by the resistance of a bath of molten slag into which dipped the graphite electrodes carrying the current. Although with such a furnace lead could be tapped from the bottom and spelter could be condensed from zinc vapor escaping from the top, the loss of zinc in the slag was prohibitive apart from other objections.

At Trollhattan, in Sweden, loss of zinc by scorification was minimized by making a high-temperature bisilicate slag, *e.g.*, 50 per cent SiO_2, but in the absence of prereduction the zinc vapor was condensed mainly as blue powder. The blue powder was melted to spelter by the ingenious Cornelius process in which by putting it in a suitably heated, revolving cylinder, oxide coatings of the zinc globules were rubbed off, thus allowing the globules to coalesce. The crude spelter thus obtained was refined by redistilling in another electric furnace. By this process many thousands of tons of spelter were produced.

Roitzheim-Remy Furnace.—In this furnace a battery of 22 annular retorts about 14 in. in diameter and about 6 ft. in height are arranged in pairs within a common combustion chamber. Inside of each retort is a vertical tube with apertures in its

walls. The material to be distilled is charged into the annular space around the central tube, the apertures of which allow the gas and vapor to escape from the retort into the tube. The two tubes of a row are connected across and thence communicate with the condenser sticking out from the wall of the furnace, which is luted in as usual. It is uninteresting to go further in description of the complicated construction of this furnace and the details of its operation.

A plant in Berlin equipped with a considerable number of these furnaces operated continuously with charges of galvanizers' ashes, which is a material not requiring prereduction and not becoming gummy when heated. Each retort received a charge of about 1000 lb. and yielded in a single tap per 24 hr. about 440 lb. of spelter plus about 80 lb. of zinc dust as ladle skimmings and prolong dust. These results were considered satisfactory.

Some trials of the Roitzheim-Remy furnace in ore distilling in other plants were unsatisfactory.

New Jersey Zinc Co.'s Process.—Success in using briquetted ore on the Wetherill grates contributed to this process of continuous distilling, in which the charge of ore and reducing coal is briquetted in the same way. Prior to charging into the retort, however, the briquettes are coked by passing them continuously through a vertical chamber of horizontal cross section in which they are coked by means of the exhausting gases from the combustion chamber of the distilling furnace, these gases entering the coking chamber at 750 to 900°C.

The distilling furnace as a unit comprises either 8 or 16 retorts. The retorts are rectangular in horizontal cross section, commonly 6 ft. × 12 in., but retorts of 7 ft. × 12 in. are in successful use. The long sides of the retort are laid up with shapes of silicon carbide carefully fitted so as to be gastight. The height of the retort that is heated is ordinarily 25 ft., but there are extensions at top and bottom for the mechanism of introducing fresh briquettes and discharging those that have been exhausted at the bottom. The retorts are operated continuously, but the charge is introduced in batches at proper intervals.

The condenser consists of two parts, the first being an inclined conduit directly connected with the retort, in which the gases are cooled rapidly, and a second part comprising a sump in which the molten spelter is collected and in which the cooling of the zinc vapor is completed at a relatively slow rate in order to avoid precipitation as blue powder by excessively rapid chilling. The condenser has baffles to zigzag the flow of vapor through it.

The exhaust gases from the condenser are scrubbed to eliminate any remains of zinc vapor and are then returned as nearly pure carbon monoxide to the combustion chamber of the furnace, thus affording 20 per cent of the heat required to fire the retort. A temperature of 1300°C. in the combustion chamber, a zinc elimination of 96 per cent, and a recovery of 92 per cent of the content of the charge may be realized. With a furnace of 16 retorts treating calcined sulphide ore of the ordinary grade of flotation concentrates, a yield of 60 tons of spelter per day may be realized. The retort life is 3 to 5 years.

The production of blue powder in the New Jersey process is very small, being only that which is scrubbed out of the gas escaping from the condenser. The coking of the charge effects preliminary reductions and reduces the production of carbon dioxide within the retort. The reduction of carbon dioxide is substantially completed in the upper extension of the retort by passing through the hot coked briquettes which likewise filter out particles of charge entrained by the gases. Any blue powder formed on the descending charge is thus automatically returned to the reduction zone of the retort. All this was a perfection of the old idea of passing the gas and vapor from the zinc retort through a filter of incandescent coke, as in the Kleeman condenser of former times.

The New Jersey continuous process has had the advantages of giving an increased extraction of zinc, less production of between products, less requirement for coal for fuel (this saving being enhanced by utilization of the carbon monoxide gas from the condensers), a saving of labor, the production of an improved grade of spelter, and the general advantages resulting from steady conditions that are capable of close regulation. On the other hand it is subject to increased cost for labor and material in briquetting the charge, and the amortization of a costly plant.

New Jersey vertical retorts are in use at Palmerton, Pa., Depue, Ill., Meadowbrook, W. Va., Avonmouth, England, and Oker, Germany. Having been first commercialized in 1929 and having been in steady use since then, this process is now thoroughly established.

The St. Joseph Lead Co.'s Process.—This process, which is the most successful of any of the proposals for electrothermic distillation, was developed from the patented ideas of E. C. Gaskill. Instead of trying to combine zinc smelting and lead smelting, as in the fusion processes of prior inventors, he conformed to the simple principle of zinc reduction and distillation with internal heating instead of external. The process as originally introduced at Josephtown, Pa., in late 1930 contemplated only the production of zinc oxide.

Calcined ore is sintered under conditions to produce an unusually hard sinter. By-product coke is used for reduction fuel. Both ore and coke are sized, then mixed in equal-volume proportions, and preheated in a revolving kiln to a temperature of about 850°C.

The preheated mixture is charged into columnar furnaces, 69 or 96 in. in diameter inside and 37 to 40 ft. over-all in height. Near the top of this shaft four or six electrodes protrude into it, and a corresponding set enters near the bottom, the height between each group of electrodes being 26 ft. Inasmuch as the charge is to be the resistor, the carbon must be constantly maintained in excess of what is required for reduction of zinc oxide. Each furnace contains upward of 25 tons of charge, and about 18 hr. is required for passage through the furnace. Internal temperature is about 1200°C. Gas and vapor escape through 12 openings, disposed in groups of three on each of four levels within the electrode boundaries, and the vapor is burned to oxide which is baghoused in the usual way.

The original Josephtown furnaces were designed only for the production of zinc oxide. Because of the relatively enormous output of zinc vapor per furnace day, it was quickly found that surface condensers of the area required would be very large. Hence, attention was turned toward developing a more compact condensing means. That problem was solved by the development of a special condenser which is described in U.S. patent 2070101, Feb. 9, 1937, issued to George F. Weaton and H. K. Najarian. This condenser is in effect a U tube containing molten spelter, just as a manometer contains mercury, but one limb is of circular cross section, being a 36-in. diameter steel tube lined with heat-conducting refractory material, connecting with the furnace and being capable of temperature control. The vertical limb leads to a gas washer of special design which is described in U.S. patent 2298139, Oct. 6, 1942, issued to Carleton C. Long and George E. Deeley. A pipe with a vacuum-control valve connects the gas-deduster discharge to a mechanical exhauster. The idea is that the gas and vapor shall be drawn through the molten spelter contained in the condenser, and that following condensation of the zinc, the gas shall be drawn through the washer. The gas bubbles through the molten zinc. Periodically, zinc is tapped from a "tapping well" which communicates with the lower part of the condenser.

The molten zinc is preferably kept at a temperature of 500 to 550°C. The vapor enters the condenser at a temperature of about 850°C. In the vapor-collecting ring surrounding the furnace there is a considerable drop of vapor temperature, but not enough to condense any appreciable amount of metal, as the dew-point temperature

is ordinarily about 830°C. The power required for operating the vacuum pump and CO compressors when condensing 100 tons of spelter per day is approximately 475 hp. Spelter assaying 99.97 per cent zinc is produced. Zinc dust recovered from the washer depends on the vapor pressure of the condenser exit gas and is about 3 to 10 per cent of the condenser production of spelter.

Spelter production is about 18 tons per furnace-day for the 69-in. D furnaces. Operating labor in the furnace plant is approximately 5.5 man-hours per ton of spelter produced. Over-all recovery in spelter and other salable products is 90 to 93 per cent. Of the loss, about 4 to 5 per cent occurs through zinc in the finally discarded residue. Total smelter power requirements are 3258 kw.-hr. per ton of zinc equivalent produced. This is for 54 to 55 per cent Zn concentrates. For higher tenor feed, recovery is somewhat higher and power requirement somewhat lower. Furnace power is 78 to 79 per cent of what is required for the entire plant operation.

It appears from these data that the use of electrothermic power at Josephtown is much less than what it was at Trollhattan, when electrothermic distilling was being performed there. One reason for the difference was that at Trollhattan the gangue of the ore was fused and run off as a slag, which was a great consumer of energy, whereas at Josephtown the gangue is discharged unfused.

Spelter Directly from Slag.—The St. Joseph Lead Co. since 1941 has been developing a method for the recovery of zinc as spelter directly from slags of lead smelting at Herculaneum, Mo., containing 12 to 16 per cent zinc. In 1944, several hundred tons of spelter were produced there by this method, and it is believed that large-scale production is imminent.

The reduction of zinc is accomplished in an electric furnace in the form of a horizontal cylinder of 1-inch steel plate, 42 ft. long by 15 ft. 4½ in. in diameter, outside dimensions, which are reduced to about 37 × 11 ft., inside, by refractory linings. Slag is fed through a small water-cooled hole in one end wall, about 12 in. above the maximum slag level, and spent slag is withdrawn through a water-cooled tap in the opposite end wall, matte and iron being tapped through a lower hole. Electric power is introduced by six carbon electrodes, 30 in. in diameter, spaced on 5-ft. 6-in. centers in line along the top of the furnace. Gas and vapor are led to a Weaton-Najarian condenser, 31 ft. long, with associated Long-Deely gas dedusters. Metal tapped from the condensers is drawn to a large settling furnace, whence spelter of Prime Western grade, containing about 1 per cent lead, is obtained.

Coke breeze, for reducing carbon, thoroughly dried, is distributed by a Deeley coke flinger over the top of the slag bath throughout its length. The depth of the slag bath, into which the carbon electrodes dip, is 10 to 30 in., the depth being measured by a bar let down through a hole in the roof of the furnace. The slag bath is the resistor. The electrodes that dip into it are raised and lowered by motor-driven staffs. The operation proceeds essentially on a continuous basis, but the feed and discharge of the slag are semicontinuous. The exit slag is about 80 per cent of the weight of the incoming slag when the latter contains 12 to 13 per cent zinc.

It is expected that in commercial operations the power consumption will be 800 kw.-hr. per ton of slag of 14 per cent zinc; the coke consumption, not over 7.5 per cent of slag weight; the electrode consumption, not over 10.5 lb. per ton of slag; stripped slag to contain not over 20 per cent of the zinc charged; and the over-all recovery as slab zinc, 75 per cent of the zinc in the feed.

Spelter Directly from Brass Scrap.—Heretofore the only method of recovering zinc from brass scrap has been to vaporize it, let it burn, and collect the oxide fume by filtration (baghouse). In the Wilkins-Poland process, recently developed, the scrap is melted and is fed into a sealed distilling furnace, which is lined internally with carbon blocks. The temperature of the furnace is raised by electric current passing

through graphite resistors. Zinc is distilled off, condensed, and cast directly into slabs. The condensers operate simply and effectively, there being no diluting gas in the zinc vapor entering into them. In starting the operation, an atmosphere of nitrogen is established in the melting furnace and the distilling furnace is flushed out with nitrogen until it becomes filled with undiluted zinc vapor. After the zinc is distilled off, the residual copper is drawn off and fire-refined in the ordinary manner. Mr. R. A. Wilkins informs me that as a matter of operating economy, it is not possible to reduce zinc to much below 2 per cent, that quantity being discharged in the copper going to the fire-refining operation. From brass scrap averaging 30 per cent zinc or more the recovery of zinc in the form of slabs is upward of 90 per cent.

CADMIUM

By W. R. Ingalls[1]

Cadmium a By-product.—Metallurgical literature has no record of any ore beneficiated for cadmium alone, and the cadmium of commerce is derived from zinc ore, with which cadmium is generally associated. Zinc ores free from cadmium, *e.g.*, the ores of the Franklin and Stirling mines, New Jersey, and of Broken Hill in Rhodesia, are rare.

Blende concentrates of 50 to 60 per cent grade have contained (in production of important tonnage) as much as 1 per cent Cd, which is unusually high. The concentrates from the Tri-State district average 0.3 to 0.4 per cent Cd, which is high. The concentrates from mines west of the Rocky Mountains seldom are higher than 0.2 per cent.

In the periodic system of the elements, cadmium is in the same group with zinc. Its properties and compounds are similar. Its metallurgy is also similar. Cadmium has a melting point of 320°C. and a boiling point of 778°C., while the melting point of zinc is 415°C. and the boiling point 905°C. These conditions, together with the lower reduction temperature of cadmium oxide, indicate a means for separating cadmium from zinc.

Cadmium in spelter is viewed, if not as an impurity, at least as an alloying element that may be objectionable, its special effect being hardening. However, for some purposes, a little cadmium in spelter is desired, and 0.4 per cent may be permissible, even in spelter for rolling. Cadmium in spelter for brass making is completely volatilized at the temperature of that process, and in bygone days an immense quantity of cadmium must have been lost in the fumes from these furnaces. The arrangement of brass mill furnaces is such that the collection of fumes is economically impracticable. At the present time, however, the brass makers are mostly using high-grade spelter (cadmium-free).

The salts of cadmium are poisonous, materially more so than are the corresponding salts of zinc. A dose of 0.03 g. of a cadmium salt is fatal to animals, and very small quantities are poisonous to human beings. Cadmium may be easily electroplated, and when so applied adheres firmly and resists bending without cracking, but it is readily attacked by acetic and tartaric acids, appreciably more so than zinc. In view of its ease of solubility and its toxicity, the use of cadmium for articles that may come into contact with foodstuffs is inadvisable.

Pyrometallurgy—Early.—Cadmium compounds, sulphide and oxide, being more volatile than the corresponding compounds of zinc, loss of cadmium begins to occur from the first furnace operation. In normal roasting, even with Tri-State ore, this loss may not be very high. Raw ore, assaying 0.4 per cent Cd, may be expected to give a roasted product of the same assay, which would imply a cadmium loss of about

[1] A condensed version of this article appears in *Trans. A. I. M. E.*, Vol. 159. 1944.

15 per cent. Roasted ore, assaying 0.4 per cent Cd when distilled at ordinary furnace temperature yielded spelter containing about half of what was in the ore charged.

The first draw of spelter under these conditions may assay 0.8 per cent Cd (accounting for 22 per cent of the cadmium recovery), and after the several draws of spelter have been equalized the cadmium content may average 0.35 per cent. If therefore 2000 lb. of blende averaging 0.35 to 0.4 per cent Cd is roasted and distilled, there may be obtained 1000 lb. of spelter, assaying 0.35 per cent Cd or 3.5 lb. content, which entering into Prime Western spelter will be sold at the spelter price.

It will be observed from the previous outline (summarizing conditions prior to the introduction of sintering) that the main loss of cadmium occurred in the distillation process and by failure to condense, which could be ameliorated by attaching a prolong to the condenser, thus collecting additional zinc dust, relatively rich in cadmium. This was the basis of cadmium metallurgy, especially practiced in Upper Silesia, prior to the introduction of the process of electrolytic zinc extraction. The primary zinc dust containing 5 or 6 per cent Cd, mixed with some charcoal, is distilled and redistilled until finally, by thus fractionating, a metal containing 99.5 per cent Cd is obtained. The low temperature of this distilling permits the use of cast-iron retorts and sheet-iron condensers, which either are lined with some refractory material or are whitewashed with lime inside so as to prevent contamination by iron.

Electrometallurgy.—With the introduction of the process of electrolytic zinc extraction in the United States and Canada in 1915-1916, that process became a large source of cadmium production, inasmuch as both cadmium and copper were bound to be leached along with zinc and necessarily had to be precipitated prior to zinc electrolysis. This purification is effected by adding zinc dust to the solution in such proportion as to throw down copper, which is filtered out and sent to copper smelting. Such a precipitate may assay 70 to 75 per cent Cu, 1 per cent Cd, and 3 per cent Zn (reflecting the excess of zinc necessarily used). To the filtrate a large excess of zinc dust is then added, and the purified liquor is filtered off, leaving a zinc-cadmium sludge.

The zinc-cadmium sludge may be stockpiled in heaps, promoting oxidation and solubility in acid; or oxidation may be expedited otherwise, *e.g.*, by spreading it on a platform and steaming it. Either way the cakes will probably have to be disintegrated, which may be accomplished by attrition in a pebble mill. There may have to be a precipitation of cobalt, requiring the use of some reagent, *e.g.*, nitroso-beta-naphthol or potassium xanthate. However, the electrolysis of cadmium sulphate solution is not very sensitive to impurities, and their removal by zinc-dust precipitation is generally adequate. It is impossible to wash all the entrained zinc from the cadmium sludge, so zinc is a cumulative impurity in the electrolytic cycle. It is controlled by precipitation with milk of lime. It is only necessary to maintain the zinc in the electrolyte at a point where the excess of cadmium over zinc in the spent electrolyte is of the order of 10 to 15 g. per l.

In the final stage of cadmium recovery, the sludge is dissolved in spent electrolyte and subjected to electrolysis either with rotating cathodes or with stationary cathodes, which are of aluminum as in zinc electrolysis. Cadmium has a strong tendency to deposit as buds, sprouts, and trees. These are obviated by the use of rotating cathodes, or with stationary cathodes when cell temperature is maintained at 30 to 35°C. and with the addition of glue to the electrolyte. A deposition of 1 lb. of cadmium per 1.04 kw.-hr. of direct current, compared with 1.5 kw.-hr. for zinc, is realized. The plant factor is of course higher by virtue of the loss in changing from alternating current to direct current and the mechanical power that is required in plant operation

In American practice, stationary cathodes are generally used and with the same cell construction and operating conditions as for the electrolysis of zinc. With

3.5-in. spacing between cathodes, the cell voltage is approximately 2.6 to 2.7 and the current density about 4 amp. per sq. ft., but in some practice it is as high as 10 amp. The cell feed may contain per liter 100 g. of cadmium, 80 of zinc, and 70 to 80 of H_2SO_4, and may be as high as 200 g. of cadmium and as low as 30 g. of zinc. Cathodes are stripped every 12 hr. in some practice, every 24 hr. in other practice. They are melted in a cast-iron pot, electrically heated to 400 to 450°C., under a thin layer of caustic soda to prevent oxidation; and the pot is well hooded to carry off oxide fume.

After the cadmium has been dissolved and is ready for electrolysis, the recovery as ingot is about 96 per cent. If the raw ore is roasted without special means for collection of dust and fume, the over-all recovery may be 84 to 85 per cent. If the roasting furnaces are connected for sulphuric acid manufacture with thorough provisions for collection of dust and fume, over-all recovery may be 90 to 95 per cent. Electrolytic cadmium is of 99.95 per cent grade, or better.

Hydrometallurgy.—In the use of roasted Tri-State ore for the manufacture of ordinary zinc lithopone, it is necessary to remove cadmium just as it is for electrolysis. Such ore has been partially decadmiumized by a water leach, but that has not been a general practice, which is rather to take out the cadmium with an acid leach. From such a solution the cadmium is precipitated by addition of an excess of zinc dust, affording a zinc-cadmium sludge. As to purification the requirements for a solution of zinc sulphate for lithopone are almost as refined as for electrolysis. The sludge obtained in this way may assay 35 per cent Cd, 46 per cent Zn, and 21 per cent water; or 54 per cent Cd, 16 per cent Zn, and 30 per cent water. These analyses vary naturally according to the excess of zinc dust that is used. The cadmium in such sludge is sold by the manufacturers of lithopone at something like 75 to 80 per cent of the price for cadmium in sticks, pencils, and other refined forms, manufacturers of cadmium pigments being the buyers. Digesting the sludge with sulphuric acid and obtaining a solution of $CdSO_4$ or $CdSO_4 + ZnSO_4$, the sulphides of those metals may be precipitated with a solution of barium sulphide to make cadmium lithopone; or a precipitate of cadmium sulphide may be thrown down from an acid solution by H_2S.

Pyrometallurgy—Recent.—When the sintering process for desulphurizing and fritting zinc ores was introduced, it was immediately noticed that the smoke issuing from the chimney dispersing the gases frequently showed the brown coloration of cadmium oxide and, concurrently, that the cadmium content of the sintered ore was reduced or even all but entirely eliminated. It was observed moreover that following the introduction of roasters of the McDougall type, roasting flotation concentrates with cyclones, improved dust-settling chambers, Cottrell precipitators, etc., as appendages, there was obtained dust and fume relatively rich in cadmium, *e.g.*, as high as 4 per cent Cd and all of it water-soluble.

An experience with an ore containing 1.05 per cent cadmium, or 21 lb. per ton, following introduction of sintering, is illuminating. From a roaster (of the McDougall type) 80 lb. of heavy dust assaying 4 per cent cadmium was collected from 2000 lb. of raw ore. There was a further settlement of fume, but 1 lb. of cadmium per ton of ore passed through the Glover towers and into the sulphuric acid. The calcines weighed 1700 lb. and assayed 0.65 per cent cadmium, and the sintered cake assayed 0.375 per cent cadmium. The first draw of spelter weighed 204 lb. and assayed 1.25 per cent cadmium; the subsequent draws, aggregating 680 lb., assayed 0.08 per cent cadmium. The cadmium accounting in terms of pounds per ton of raw ore was as in the table on page 472.

It is clear that nearly all the cadmium in this ore could be recovered by providing suitable means, especially for expelling all the cadmium from the calcines (leaving none to go into the retorts) and collecting all the dust and fume from both the roasters and the sinterers. In the experience here summarized the volume of gas from the

sinterer was 462,000 cu. ft. at 218°F. per ton of calcined ore, which could have been greatly reduced by sealing the side openings between pallets and wind box (see the chapter on Pyrometallurgy of Zinc).

In flue dust from roasters	3.2
In fume from roasters	5.8
In sulphuric acid	1.0
Loss in sintering	4.6
Content of first draw of spelter	2.6
Content of subsequent draws	0 5
Content of blue powder	0.5
Content of retort residue	0.2
Escape from condensers, by difference	2 6
Total	21 0

These observations became the basis of the improved metallurgy among zinc distillers, who in view of the increased demand for cadmium after 1935 aimed to recover the large cadmium content of Tri-State ore that previously had been wasted. In order to accomplish this, the process of sintering was adjusted so as to increase the elimination of cadmium, especially by preventing its condensation in the lower part of the bed on the pallets after it had been volatilized from the upper part, this being largely a matter of temperature control and technique. It was found also that by the addition of sodium chloride, anywhere from 0.5 up to 2.5 per cent, the well-known chloridizing reaction could be realized, with nearly complete elimination of both cadmium and lead. Another expedient was moistening the ore with a solution of zinc chloride.

These proposals were founded on the idea of decadmiumizing and deleading zinc ore with the objective of producing high-grade spelter. At this time, about 1930–1933, cadmium was in poor demand. Later it became worth while for zinc smelters to save cadmium that they had previously been wasting. This involved naturally a reduction of the volume of the sintering gases by better sealing of the wind box and precipitation of their fume by means of Cottrells.

In works practice the dust and fume from the roasters in oxidized form and the dust and fume from the sinterers, containing cadmium chloride, lead chloride, and any of the excess of zinc chloride that has been volatilized, are mixed and digested with sulphuric acid. Lead sulphate is filtered off. Cadmium may then be precipitated by the addition of zinc dust, and the filtrate containing zinc sulphate and zinc chloride is returned to the sintering process, while the cadmium precipitate is refined by distilling, or otherwise.

By the New Jersey process of refining spelter by redistillation, cadmium comes off in the form of cadmium-zinc metal or a cadmium dust, which is readily converted to metallic cadmium by any one of the several known methods. This was done prior to the war at Duisburg, in Germany, by the Thede and New Jersey processes in combination.

In addition to the methods already described, there is a good deal of cadmium produced by the silver-lead smelters, which in treating zinc ore obtain considerable quantities of cadmium in their flue dust. Treatment thereof for cadmium recovery has been sufficiently suggested without going into details.

Out of the production of metallic cadmium in the United States in 1941, aggregating 3220 tons, the electrolytic producers in Idaho and Montana afforded 970. There is also a considerable production of cadmium that is obtained as direct chemical compounds, especially cadmium sulphide, for which there is use as a pigment, either as such alone or in cadmium lithopone.

CHAPTER XVI

MERCURY

By Gordon I. Gould[1]

History and Mines.[2]—Quicksilver, or mercury, seems first to have been mentioned by Aristotle, who referred to it as fluid silver (*argyros chytos*). Theophrastus, about 315 B.C., states that quicksilver is obtained from cinnabar rubbed with vinegar in a brass mortar with a brass pestle. Dioscorides, about A.D. 50, appears to have first mentioned the recovery of quicksilver (which he called *hydrargyros*, liquid silver) by distillation, stating, "An iron bowl containing cinnabar is put into an earthen vessel and covered over with a cup-shaped lid smeared with clay. Then it is set on a fire of coals, and the soot which sticks to the cover when wiped off and cooled is quicksilver." Pliny, about A.D. 50, reports both these methods. Agricola in his "De re metallica"[1], published in 1554, gives the first detailed description of several methods in use at that time, all distillation processes.

Although recorded production data are comparatively modern, Becker[2] estimates production in terms of 75-lb. flasks up to A.D. 1700, and thereafter with greater accuracy up to 1886. Since that time, fairly accurate records are available. Up to 1700, he estimates the world production as approximately 1,800,000 flasks; between 1700 and 1800 an additional 2,375,000 flasks were produced; from 1800 to 1900 Becker's estimate plus more accurate records indicate approximately 5,890,000 flasks; from 1900 through 1940, it is estimated that an additional 4,560,948 flasks were produced The estimated total world production, therefore, approximates 14,625,000 flasks; although other authorities have reported it to be as high as 18,000,000 flasks.

It is interesting to note that the Almaden Mine in Spain has probably been responsible for more than one-third of the total production and the Idria Mine in Italy approximately one-quarter of the total production. Other large producers include the Santa Barbara mine in Peru, the Abbadia San Salvatore mine in Italy, the New Almaden mine and the New Idria mine in California, and the mines of the Chinese province of Kwei-Chau. Although quicksilver production in recent years has come from no less than 20 countries, Spain and Italy continue as the largest producers (approximately 70 to 80 per cent combined), with the United States third and Mexico and Canada following.

Within the United States many new mines have been discovered during the past few years under the impetus of increased prices and wartime demand; however, by far the larger part of production continues to come from the older mines and probably will continue to do so. This situation also exists throughout most of the rest of the world, although important recent discoveries have been made in Canada.

Production and Prices.—Table 1 indicates the widely fluctuating production and price range that is characteristic of the industry, even before the years cited.

This wide range of price has played an important part in governing the size of the quicksilver industry within the United States, where the ores treated are of much lower grade than in other countries. Only 10 mines contributed to the total American

[1] Consulting engineer, San Francisco, Calif.

[2] References in brackets are to similarly numbered references in the Bibliography at the close of the chapter.

production in 1922, whereas there were 197 producers in 1941. Likewise, the development of ore reserves, metallurgical progress, and long-range planning have been handicapped by the wide fluctuation in price and by market manipulation by foreign producers controlling the bulk of production.

TABLE 1.—PRODUCTION AND PRICES OF DOMESTIC QUICKSILVER, 1910–1944

Year	Production[a]	Price[a]	Year	Production[a]	Price[a]	Year	Production	Price
1910	20,330	47.69	1922	6,291	59.74	1934	15,445	73 87
1911	20,976	47.16	1923	7,833	67.39	1935	17,518	71.99
1912	24,734	43.03	1924	9,952	70.69	1936	16,569	79.92
1913	19,947	40.07	1925	9,053	84.24	1937	16,508	90.18
1914	16,330	48.95	1926	7,541	93.13	1938	17,991	75.47
1915	20,756	88.17	1927	11,128	118.16	1939	18,633	103 94
1916	29,538	127.16	1928	17,870	123.51	1940	37,777	176 87
1917	35,683	107.72	1929	23,682	122.15	1941	44,921	185 02
1918	32,450	125.12	1930	21,553	115.01	1942	50,846	196 35
1919	21,133	93.38	1931	24,947	87 35	1943	51,929	195 21
1920	13,216	82.20	1932	12,622	57.93	1944	22,100[b]	126.17
1921	6,256	46.07	1933	9,669	59.23			

[a] Production and price figures for the years 1910–1926 calculated to the 76-lb. per flask basis from the 75-lb. flask then used.

[b] Estimated production, first six months 1944.

All prices are based on the average monthly quotation of *Engineering and Mining Journal*, New York.

Properties and Uses.—Quicksilver is the only metal that is liquid at all ordinary temperatures. (Gallium melts at 30.1°C.) This fact quite naturally was responsible for many early conjectures as to its true nature and, as well, gave it a rather mystic position in the hands of the early alchemists. Today, the same property makes it useful, if not indispensable, in many applications in industry, the sciences, and everyday use.

Quicksilver, the metal, has an atomic weight of 200.61, a valence of either 1 or 2, and a specific gravity of 13.595 at 4°C. The melting point is −38.85°C., below which it is a white malleable ductile metal. The boiling point is 357.25°C., above which it is a colorless vapor having a density of 6.7 to 7.03. As a metal, it has relatively low thermal and electrical conductivity and is soluble in nitric acid, aqua regia, and hot concentrated sulphuric acid, but is not soluble in hydrochloric or dilute sulphuric acid.

In chemical combination, it has a wide variety of uses. Although most of the salts are consumed in relatively small quantities, the bichloride (corrosive sublimate) and the chloride (calomel) are used in substantial quantity. Accurate information as to the specific uses to which quicksilver is put is neither compiled regularly nor is it probably very accurate; however, Table 2 shows in a general way the distribution and trend of the various uses. All figures are submitted by the authors as estimates, and it must be pointed out that the first two and the last two years cited represent wartime distribution. Especially in 1942 and 1943, this undoubtedly accounts for the large undistributed quantity listed under Other.

It is stated that half or more of the quantity shown under Redistilled for 1942 and 1943 was used in industrial and control instruments. In 1928, the dental preparations included at least some of what would otherwise be classed as redistilled.

TABLE 2.—ESTIMATED DISTRIBUTION OF USES OF QUICKSILVER

	1917[a]	1918[b]	1928[c]	1942[d]	1943[d, e]	%[f]
Pharmaceuticals			5,493	8,088	14,192	28.37
Dental preparations			362	1,198	533	1.07
Chemical preparations			7,486			
Seed disinfectants			365	1,533	1,340	2.67
Drugs and chemicals, total	8,500	12 180	13,706	10,819	16,065	32.11
Fulminate	4,850	12 218	6,587			
Vermilion	3,130	1 900	2,450			
Felt manufacture	1,700	800	1,720	20		
Amalgamation	850	800	453	180	22	0.05
Antifouling paints	3,000	905		1,220	2,578	5.15
Electrical apparatus	2,700	687	556	4,550	2,988	5.97
Industrial and control apparatus	630	676	996	3,529	3,365	6.73
Catalyst (in electrolytic preparation of caustic soda and chlorine or glacial acetic acid)			1,000	3,802	4,679	9.35
Redistilled				6,175	4,925	9.84
General laboratory use			623	294	331	0.66
Other, or not above classified or combined	1,000	1 000	2,846	17,148	15,077	30.14
Total	26,360	36 166	34,942	47,737	50,030	100.00

[a] RANSOME, Quicksilver *U.S. Geol. Survey*, "Mineral Resources of the United States," part I, 1917, p. 384.

[b] RANSOME, Political and Commercal Control of Mineral Resources of the World, U.S. Dept. of the Interior, No. 4.

[c] SCHUETTE, Quicksilver, *U.S. Bur. Mines Bull.* 335, p. 147.

[d] Mineral Market Reports, Mercury in 1943, *U.S. Bur. Mines*, No. MMS 1141, p. 3.

[e] Includes only January-November, 1943.

[f] Percentage of total consumption, January-November, 1943.

The use of quicksilver in the felt-manufacturing industry has been largely displaced, owing to the health hazard and state prohibition of the further use of the skin-irritating mercuric nitrate; amalgamation has further and further been replaced by other precious-metal beneficiation processes (and the current wartime restriction order prohibiting the operation of gold mines); the fulminate consumption has been largely reduced owing to satisfactory substitution in military requirements; and antifouling paints continue at about the same pace, though resisting substitutes have been devised.

Electrical apparatus has probably shown a greater increase than is apparent in the figure for 1943, and industrial and control apparatus is increasing greatly; general agricultural uses and requirements by the textile industry may well advance in the near future in consumption of the organic mercurials.

Although there are many uses and many industries in which quicksilver has been substituted for or otherwise displaced, there have been a far greater number of new uses developed, the aggregate consumption of which indicates a gradually increasing demand for the metal which undoubtedly assures the requirement for increased production. This increased production will have to come from lower grade ores, and metallurgical efficiencies will necessarily have to be kept at the highest possible point.

Metallurgy of Quicksilver.—Although the metallurgy of quicksilver is probably one of the simplest, it has undoubtedly been subjected to as many variations as that

of the more refractory metals. The treatment processes are first limited in that there is only one important ore mineral. This mineral is cinnabar which is the sulphide (HgS), a bright vermilion mineral. Although varying from a bright vermilion color through brownish reds to near black, it always shows the bright vermilion color on a fresh surface or by streaking. It contains 86.2 per cent quicksilver and 13.8 per cent sulphur; the specific gravity is 8.0 to 8.2; the hardness is 2 to 2.5; and the sublimation temperature is approximately 580°C. A far less important (though rather common at some mines) mineral is metacinnabarite, a mineral of exactly the same composition but differing in crystal form; this is always brownish black to black in color. Native quicksilver is not at all uncommon, though seldom occurring in quantity in any mine. Cinnabar, metacinnabarite, and native quicksilver are the prime contributors to all mercury production, except that at the Huitzuco mine in Mexico the metal is obtained from livingstonite, the double sulphide of antimony and quicksilver. At a few other mines the occurrence of the oxide, chloride, oxychlorides, and other rarer minerals, or combinations with some lead or zinc minerals, has been shown.

Cinnabar has been found in many rock types, a factor of considerable importance to the treatment of the ore. Substantial deposits have been found in sandstones, shales, limestone, serpentine, andesite, rhyolite, opalite, and tuff. The variety of host rocks and their differences in physical characteristics and accessory or secondary minerals must be well understood in order to assure efficient treatment.

The most important factor limiting the number of treatment processes is the low sublimation temperature, above which the quicksilver is volatilized and may be recovered by condensation. The fact that this operation may be performed relatively cheaply with an excellent metallurgical recovery and yield a very high-purity metal in one operation puts all combined processes (since they must all eventually roast to make final recovery) at a distinct disadvantage.

Consequently, from the pre-Christian era, the roasting of quicksilver ores has been not only the most popular but, for the most part, the most efficient method of recovery. There have been, however, several other methods used, including a variety of gravity concentration plants, several flotation plants, gravity and flotation combined, and a few chemical plants. These methods are briefly explained, following a description of the more popular roasting methods.

The Roasting of Quicksilver Ores.—The roasting of quicksilver ores depends on raising the temperature to near or above the sublimation temperature of cinnabar, at which point the quicksilver is volatile (as mercuric sulphide vapor) and subject to condensation and collection. The process, therefore, is divided into two distinct operations, *i.e.*, (1) volatilizing the quicksilver and (2) condensing and collecting it. The furnace or retort and the condenser, therefore, are the principal items of equipment, although more or less auxiliary equipment is required to complete the operation and will be discussed in their order.

Retorts.—The retort is the simplest form of recovery plant for treating quicksilver ores, and inasmuch as it requires in addition only a simple condenser and simple firing equipment, it will be described as a complete unit. Retorting is distinguished from furnacing in the fact that retorted ore is heated indirectly, whereas furnaced ore is heated directly with the gases of combustion.

The popular retorts treat one batch of ore at a time in a cast-iron pipe of various shapes. The ore, upon heating, gives forth its mercuric sulphide vapor from which the sulphur must be oxidized to permit the subsequent cooling and condensation of the volatile quicksilver. In most operations, air is depended upon to supply the necessary oxygen and is supplied to the inside of the retort by either natural or induced draft. In the former case, the air circulates by convection, in through the condenser pipe over the bed of ore and out through the same condenser pipe. In the latter case,

the air is usually blown in through the end of the retort opposite to the condenser-pipe outlet, from which it travels over the ore and out the condenser pipe. Other designs of continuous-operation retorts often depend on leakage of air through an ore seal to provide sufficient air for the oxidation of the sulphur.

Under these conditions, the chemical reaction taking place is

$$HgS + O_2 = SO_2 + Hg$$

In treating some ores containing relatively large amounts of sulphur as in high-grade ores, ores containing considerable amounts of pyrite, marcasite, stibnite, etc., it is sometimes desirable to add a flux to assist in the oxidation of the sulphur. This may be lime or iron filings or scrap, the former being more commonly used. When such a flux is used, the reaction is

$$4\ HgS + 4\ CaO = 3\ CaS + CaSO_4 + 4\ Hg$$

or

$$HgS + Fe = FeS + Hg$$

The addition of such a flux is quite necessary in high-sulphur ores in order to free the volatile quicksilver. It is not uncommon, in an improperly ventilated or underfluxed retort operation, to find the formation of synthetic cinnabar, often as long acicular crystals, in the condenser pipe. Similarly, free sulphur may also be deposited and cause additional difficulties in cleaning up the product.

Because the retort is simple, there have been numerous designs. Retorts were one of the earliest devices used for the recovery of quicksilver. Duschak and Schuette[3] report that clay retorts were used at the Idria mine until 1641, when metal retorts were first used. Modern retorts, however, include three general types, each varying according to the manufacturers, who are often the small operators.

The D retort consists of a cast-iron body designed to be set horizontally and on the flat side of the D, *i.e.*, ⌓. The common size is 20 in. across the bottom by 12 in. high and 8 ft. long. Wall thickness is 1¼ to 1½ in. It is closed at one end, and the other end is flanged to take the head, which adds another foot to the length and contains a side exit with flange for a 4-in. cast-iron pipe. The head bolts to the body of the retort and is provided on the front with a recess to accommodate a cast-iron door, securely held in place by a yoke and screw or iron wedges. The heads can be built with either right- or left-hand exits so that they may be set side by side in pairs. To the flanged exit, a cast-iron pipe usually 4 ft. long starts the condenser. To the end of this pipe, set on a slight downward inclination, is screwed or flanged a 4-in. iron cross, and another 4-in. pipe about 8 ft. long inclines downward but parallel to the body of the retort. The other two outlets in the cross are plugged but provide outlets for cleaning. This piping constitutes the average condenser; however, the long condenser pipe may discharge into a concrete box, a system of small tanks, or other devices deemed necessary by the operator to increase the efficiency of his condenser. The condenser pipes are air-cooled or may be water-cooled by dripping water on sacks laid over the long pipe or by more elaborate systems of water-jacketing the pipe.

The retort body and head are set up in a brickwork about 5 × 10 ft. in plan, the bottom of the retort being about 3 ft. 3 in. above the working floor. For heating, a firebox is built into the brickwork at the end opposite the retort door and condenser-pipe outlet and under the retort. The firebox may be designed for wood, fuel oil, or other fuels. A small flue leads the gases of combustion from the firebox toward the feed end of the retort, and at the head two vertical flues carry it upward to the elevation of the retort. It then travels back over the top of the retort body to the fire end of the retort, thence vertically upward through a stack. It is common practice to

use 3 to 6 in. of firebrick, tile, or sand insulation between the lower flue and the bottom of the retort body to protect it from excessive heat, but on the return the bare retort is exposed to the gases of combustion. Although the usual retort body and head are made of cast iron, they have been successfully made of chromium iron with varying chromium content. These have the advantage of resistance to corrosion by the sulphurous gases, as well as oxidation, and are better able to withstand overheating without damage.

In operation, the ore or other material is usually, but not always, charged in three or four steel pans to facilitate charging and discharging the material. Material charged should not exceed 1½ to 2 in., and on finer material the capacity must usually be decreased or the burning time lengthened. On relatively clean ore without excessive fines, a charge of 750 to 1000 lb. can be charged to the retort every 12 hr., giving it a daily capacity of ¾ to 1 ton per 24 hr. If they are set up in pairs, the unit would have double this capacity. Although a few retorts have been equipped with thermometers, they are usually operated by observation through peepholes in the brickwork, the retort being kept at a dull red heat by manipulation of a damper in the stack. Operating in this manner usually consumes about ½ to ¾ of a cord of wood or 25 to 35 gal. of fuel oil per day. These quantities are subject to variation in operation, character of wood fuel, and character of material being treated. If oil-fired, the burner usually consists of a relatively simple oil burner of the low-air-pressure atomizing type, or an oil mantle burner.

The cost of the ironware described above, plus steel buckstays for the brickwork, stack and fire door and frame, for a double unit is approximately $1200. About 3250 common red brick and 4000 firebrick are used in setting up a double-D retort. Together with oil-firing equipment, the estimated cost of such a unit is $2500 to $3000, depending on location, etc.

The Johnson-McKay type of retort consists of a battery of round cast-iron pipes, usually 12 in. in diameter by about 6¼ ft. long. Although the standard setup usually included 12 pipes, they have, in various installations, ranged from one pipe up to a dozen or even more. They have, likewise, been made of pipes of varying dimensions; however, in principle they conform. The pipes are set horizontally and like the D retorts are closed on one end except for a hole to receive a 3-in. condenser pipe, 8 ft. long, which inclines downward. The front end of the pipe includes a bell with a double shoulder to receive two lids which are luted in place with mud or wet ashes, the outer door being more securely held in place, usually by a bar and wedges. The condenser pipes are most often cooled similarly to the method described for the D-retort condenser pipes.

The pipes are supported in a brickwork which, however, is quite different from the D-retort structure. In the D retort the heat passes from the back of the retort to the front, up and back over the top of the retort to the back, and out through a stack. In this type of retort, a firebox is built at one side and for the length of the pipes and the heat passes through several flues under the pipes and at right angles to them for as many pipes as there are in the unit; it then rises to an elevation above the pipes and returns over them to the upper part of the firebox where it is exhausted through a stack. Similar practice is followed in protecting the lower part of the pipes by insulation from the lower flues, although the upper portion of the pipe is exposed to the direct heat.

In operation, the ore is charged by long-handled scoop shovels directly into the pipe and discharged by hoeing out the burnt ore. From 250 to something over 300 lb. of ore can be charged to each pipe, thus giving a 12-pipe unit a capacity of about 1½ to 2 tons per 24 hr., charging each pipe twice a day. This is usually performed by charging one pipe each hour, making two cycles per day. The wood consumption

is roughly 1 to 1½ cords per day, so that by comparison with the double D retort, approximately twice the amount of fuel is required. This is easily understood in the more compact construction and the use of larger pipes in the D retort.

Except for installations of one, two, or possibly three or four pipe units, no retorts of this type have been built in recent years, so that estimates of cost might be rather inaccurate; in any event, it would considerably exceed the cost of the more popular D retort. The smaller installations that have been made have often been cheaply and poorly built and represent only an attempt to "get by cheaply."

A third type of retort, which though very much underdeveloped has been popular during the past few years for prospecting or for small operations, is the inclined-pipe retort. It has been built in a variety of sizes and by nearly as many designers as there are users; however, they are all similar in principle. Most of the units have been constructed of pipes, either cast iron or standard steel, ranging in diameter from about 10 to 16 in. and in length from about 6 to 12 ft. The pipes are set up on a 45-deg. incline and are fed at the top and discharged at the bottom, the discharge being accomplished by raising a door and allowing the material to slide downward through the pipe. Although practice varies, an ore charge is usually left in the pipe for 8 to 12 hr., then the whole charge is withdrawn and a new batch fed in through the top. Feeding at the top of the pipe may be by hand shoveling or by chute from a small ore bin, and the top seal usually consists of an iron plate luted to the pipe with clay or wet ashes.

Near the top of the pipe, a condenser outlet pipe 2 to 4 in. in diameter is cut into the pipe to provide for the exit of the quicksilver vapors, and because air is admitted through an ore seal at the lower end of the pipe, the gas volume (air) through this type of retort is usually considerably more than in other types of retorts. Consequently, more elaborate condensers are used and usually have consisted of various styles of piping of small diameter (2 to 4 in.) with wooden barrels, tanks, or other settling chambers interspersed.

Because of the slope given to the pipe and the fact that this feature lends itself to construction on a side hill, this retort has often been referred to as the "side-hill retort." They are often built in multiple units up to four in a group and are so designed that a masonry pier supports the upper and lower ends of the pipes. Side walls with one or more arches of clay, rock, or brick, over the pipes, provide a shell around all the pipes, and a grate is built behind the lower pier and under the pipes. Fuel of all types has been used, and the heat circulates up and over the pipes to the upper end of the pipes, where it is allowed to escape to a damper-controlled stack.

By their very design, this type of retort is capable of a greater capacity than the horizontal-pipe retorts; however, the absence of good design in the firebox and enclosing shell has resulted in poor distribution of heat with consequent reduced capacity or, more often, incomplete roasting of the ore and reduced recovery. The variety of sizes and designs precludes the possibility of making accurate cost estimates on this type of retort, although they have mostly been cheap installations. If designed and constructed with the same care and materials as are used in the other types mentioned, it seems probable that their cost per unit of capacity would be about the same. Fuel consumption is high, although this might be materially improved with sound design.

Although these three types of retorts represent the most commonly used types, there are many others ranging from pot stills to single and multiple rotary retorts of elaborate design. Few, if any, of these have gained as much favor or stood the test of operation as well as the types described above.

The retort, as has been shown, is a small reduction plant, high in cost per unit of capacity; although subject to many variations, it can be made to operate quite

efficiently. An objectionable feature of all retort operations is the manual charging and discharging operation, which causes exposure to quicksilver fumes. Many arrangements and many devices including hoods, blowers, lids, respirators, and other protective devices have been tried, but the retort continues to subject the workman to the fumes, causing salivation. The substantial portion of production is made in the larger furnace units, but there will probably always be a place for the retort. They are cheaply installed by the small operator, either as a production unit or as a prospecting tool; they are used occasionally by the furnace operator to assist in cleaning up mud and soot; or they are used to retort concentrates from milling operations. In the chemical field, they have a very definite place in the recovery of secondary quicksilver from scrap or in reclaiming the metal from mercurial salts.

Furnaces.—The treatment of quicksilver ores in furnaces differs from retort operation, as previously stated, in that the heat is applied directly to the ore and the gases of combustion are combined with the volatile products liberated by heating the ore. In contrast to retort operation, where only a small amount of air is available for oxidation of the sulphur, furnace or direct-fire treatment of the ore makes available larger quantities of air. The amount available as excess over requirements for combustion of the fuel, therefore, is of extreme importance. It must provide sufficient oxygen to combine with all the sulphur released by the cinnabar or other sulphides which may dissociate within this temperature range and to combine with certain other volatile elements such as arsenic or antimony. Any larger quantity only requires additional fuel for heating and increases the volume of gases to be handled. In practice, it is necessary to maintain an excess over theoretical requirements in order to assure contact and a sufficient volume for sweeping the quicksilver vapors from the furnace. In addition to this difference, furnace treatment usually infers greater capacity and continuous operation.

Although it was probably not the first furnacing operation, as above defined, López Saavedra Barba is given the credit for inventing, or at least first applying, the shaft type of furnace to the treatment of quicksilver ores. This was in 1633 at the Santa Barbara mine in Peru. The success of this type of furnace led to its introduction at the Almaden Mine in Spain by Bustamente, where a number of them were built within the next twenty-five years. They have since acquired the name Bustamente furnace, and many of these original installations, now 300 years old, are still in use.

Furnaces built up to 1916 (with only a few exceptions thereafter) are generally referred to as the "brickwork furnaces," because of the massive brickwork necessary to contain them. Since that time, the "mechanical furnaces" have taken over and are today the only type in use.

The brickwork furnaces were of several designs, originating probably with simple shaft furnaces. This design was later modified, and the shelf or tile furnaces became more popular owing largely to the requirement for treating fine ore. A tabulation of furnace types follows:

Brickwork furnaces

1. Intermittent type.
   - *a.* Simple shaft furnace.
   - *b.* Bustamente, invented in Peru, 1633, and developed at the Almaden in Spain.
   - *c.* Neat.
2. Continuous type.
   - *a.* Exeli, developed at Idria, 1872.
   - *b.* Knox-Osborn, developed in California from 1872.
   - *c.* New Idria Coarse Ore, developed at New Idria, 1900.

d. Spirek, developed at Idria about 1910.
e. Kroupa, developed at Idria about 1915.

3. Shelf or tile furnaces.
   a. Knox & Osborn, developed in California, 1870's.
   b. Huttner-Scott, more popularly called the Scott, developed at New Almaden, 1875.
   c. Cermak-Spirek, developed at Idria, 1886.
4. Side-hill furnaces.
   a. Livermore.
   b. Fitzgerald, more properly a large side-hill retort.

Mechanical furnaces

1. Rotary furnace, developed at New Idria, 1916.
2. Multiple hearth furnace, developed at New Almaden, 1916, more popularly referred to as the Herreshoff.

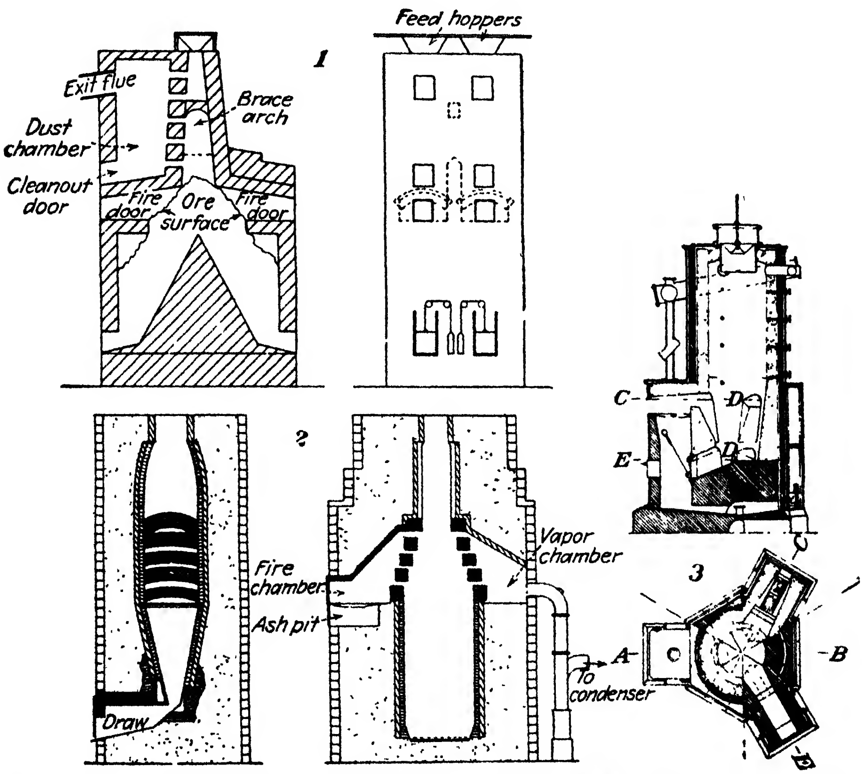

FIG. 1.—Coarse-ore furnaces: *1*, New Idria type; *2*, Knox & Osborn; *3*, Exeli iron-clad.

While this is not a complete list of all furnace types, it represents the more soundly designed furnaces and those which have a production background. It represents the plants used not only in the United States but also in Spain, Italy, and other quicksilver-producing countries of the world.

Furnaces listed under Brickwork furnaces, 1, 2, and 4, were all designated as coarse-ore furnaces. All those under 1, also 2*d*, contained their fuel within the ore charge, and in those of the intermittent type the furnace was charged with a layer of ore and a layer of fuel until filled, the charges fired, and it was allowed to burn out.

The gases containing the quicksilver vapor were drawn off the top into condensers (to be discussed later under that heading). After the fuel had burnt out, the furnace was

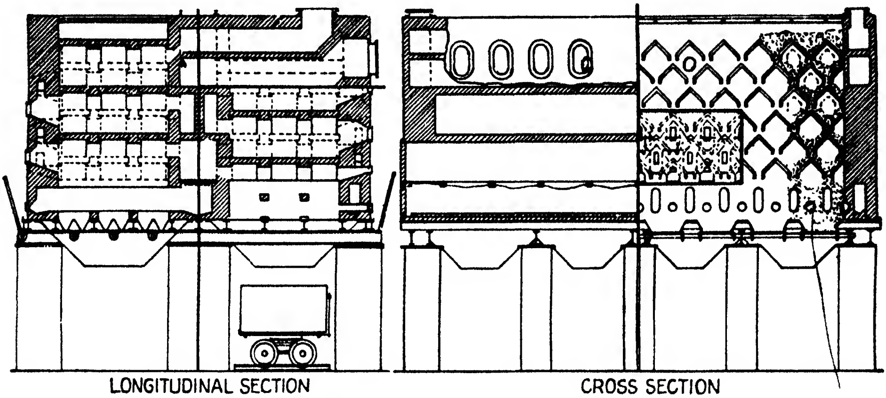

FIG. 2a.—Fine-ore furnace (Cermak-Spirek).

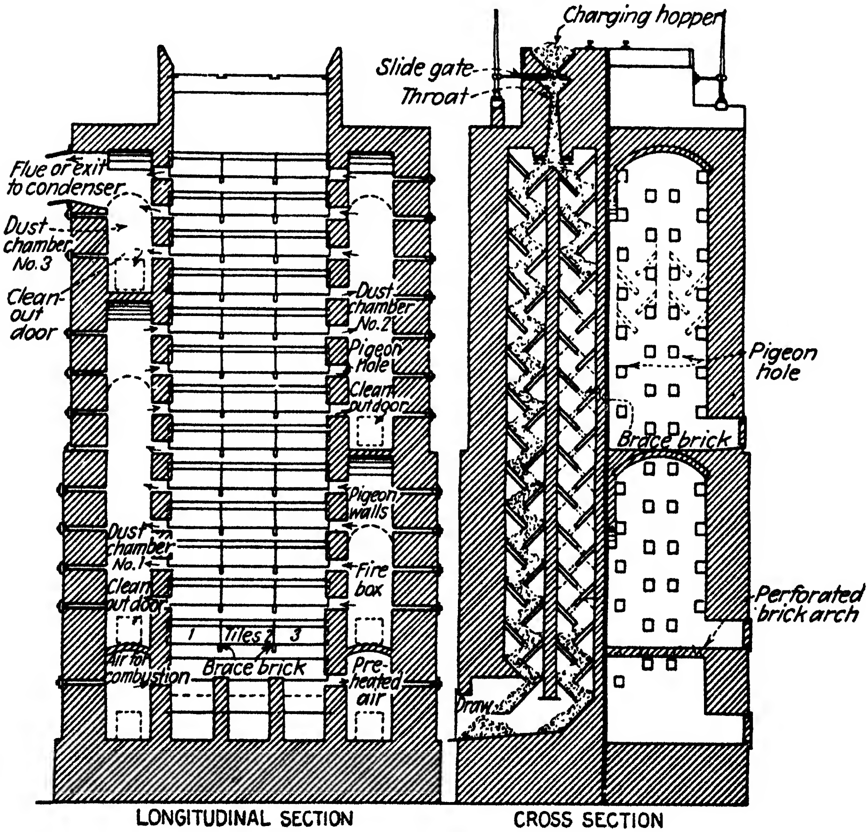

FIG. 2b.—Scott shelf furnace.

allowed to cool, the charge withdrawn, and the shaft recharged. Cuts of these furnaces are shown in Figs. 1, 2, and 3.

The change to the continuous-type furnaces in the '70's was required in order to gain greater capacity for the treatment of lower grade ores and the large demand for quicksilver for amalgamation by the gold-producing industry (in the United States). Although considerable change in design was required, the principle remained the same as in the earlier shaft furnaces. For the most part, it meant arranging suitable gates, rakes, or doors for intermittently drawing off a portion of the roasted ore, providing for suitable charging doors at the top of the furnace, and adding a firebox, either near the bottom of the furnace or part way up (New Idria coarse-ore furnace), as most of these furnaces depended on the application of heat from an external source. Kilns of the shaft type as under 1 and 2, being made of heavy brick walls and requiring a minimum gas-volume travel through the charge, had relatively high thermal efficiencies but were not suitable for larger capacities. For best operation, the ore had to be *all* coarse; else the fines would fill the interstitial openings and blind off a section of ore from heating. This feature together with a requirement for a relatively dry feed, in part, led to the development of the shelf or tile furnaces listed under 3.

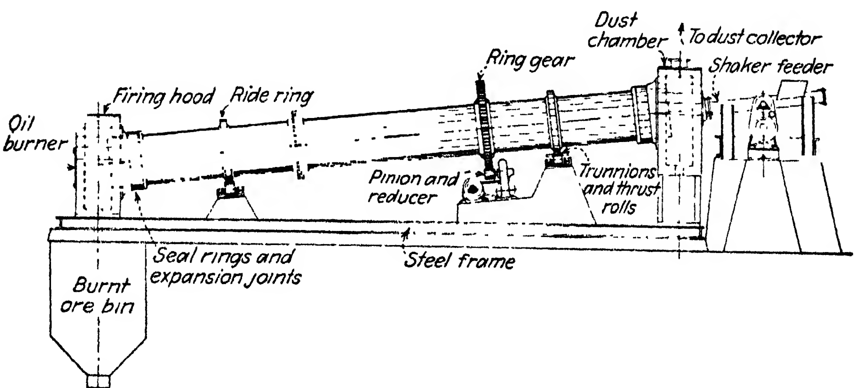

Fig. 3.—Rotary furnace

The three furnaces, here listed, are all known as fine-ore furnaces and, in addition to the reasons just pointed out, were developed because of the need for a furnace to treat the fine ore made in blasting for larger scale production. It was the custom at the older plants, where only coarse-ore furnaces were installed, to make adobes of the fines produced in cobbing or sorting. The adobes were made by mixing the fines with local mud into bricks (several sizes, though mostly about the size of a common brick) and sun-drying them. As the quantity of fines increased, this obviously became an expensive procedure, and there developed the need for a furnace to treat fine ores.

Although there was reputedly no collaboration or connection, one with the other, the three furnaces utilized the same principle in permitting ore to pass downward through a shaft furnace thus keeping it from packing, to prevent blinding. This was accomplished in the Knox-Osborn and in the Scott by feeding the ore at the top of the furnace into one or more shafts, in which tile set at an angle of 45 deg. and staggered was set in the side walls. The ore pursued a zigzag course downward from one tile to the next, the tiles being set 3 to 6 in. from each other at the edge. Peepholes permitted observation of the course of the ore as well as rabbling, should it hang up between tiles.

The essential difference between the Knox-Osborn and the Scott was in the firebox and the course of the hot gases through and over the ore. In the Knox-Osborn, a firebox the height of the shelf system was built on one side of the furnace. The gases traveled horizontally across the furnaces, under the tiles and over the ore, to two chambers on the opposite side. In these, the dust settled and the gases, including the quicksilver vapor, were drawn off. In the Scott furnace, a low firebox on one side was used. Hot gases from the firebox traveled across the furnace, as in the Knox-Osborn, but only under the bottom two or three tiles. At the opposite side, a chamber received these gases and reversed their direction so that they again traveled across the furnace, but in the opposite direction and the next two or three tiles higher. There a similar chamber again reversed the direction for heating higher tiles, and so on, depending on the height of the furnace. At the top, the gases leave the furnace for the condensing system.

The Cermak-Spirek furnace, developed at the Idria mine in 1886, is similar to the above two types as to ore flow except that, instead of the flat tiles used for changing the direction of the ore, a pyramided arrangement of gable tiles accomplishes the same purpose. In regard to heat flow, it is similar to the Knox-Osborn and, unlike either furnace, it is usually built lower and with more tiles.

Mechanical Furnaces.—The previously described furnaces are distinguished from the so-called "mechanical furnaces" largely by the lack of machinery required in their operation. About the only mechanical equipment required (and it was not always used) was an exhaust fan for drawing the quicksilver-laden gases from the furnace and through the condensing system and, at the same time, creating an adequate draft over the firebox for good combustion.

The development of mechanical furnaces was possibly delayed (by comparison with the mechanization of other metallurgical processes) because of two principal factors: (1) the brickwork manually operated furnaces made an excellent recovery when properly operated; and (2) the average quicksilver operation was small, subject to wide fluctuations of the market, and, consequently, usually not financially able to experiment with more expensive and complicated equipment.

In 1916, under demand created by the Second World War, it became apparent that larger tonnages of lower grade ore would have to be treated. It would not have been feasible to attempt to increase the size of the then popular Scott furnaces, and the break away from the brickwork furnaces began.

Although various types of mechanical furnaces have been built, the successful types are the rotary furnace and the multiple-hearth type furnace.

The rotary furnace is by far the most popular type in present use and has gained this popularity largely through its low initial and operating cost, its great flexibility and ease of control, and in most cases by considered design by the manufacturer to meet conditions encountered at the individual mine.

Three early attempts were made to apply the rotary furnace to quicksilver ore reduction although it was suggested as early as 1876. The first attempt was made at the Socrates mine in California in 1903, the second at the Aurora mine in California in 1911, and the third at the Abbadia San Salvatore mine in Italy in 1913. Of the first two operations, little is known; however, their failure to remain in operation probably indicates their lack of success. The Italian operation has been well described by Duschak and Schuette[3], who outline the difficulties encountered and later overcome to a certain extent.

The beginning of the rotary furnace, however, may be dated from 1916 at the New Idria mine in California. At this property, an experimental furnace was installed in that year, and in the year following four larger furnaces were installed. The

successful operation of these furnaces led to their further development and many subsequent installations.

The multiple-hearth type furnace was first applied to quicksilver ore reduction also in 1916 at the Senator mine in California and the Goldbanks mine in Nevada. Furnaces of this type, known as the McDougal, Herreshoff, or Wedge furnaces, had been successfully used in many other types of roasting operations so that the application to quicksilver ore reduction was mostly a matter of adjustment of operating conditions rather than a change of basic design.

In both types of mechanical furnaces, a continuous flow of ore passes through the furnace, and while the ore is in the furnace, it is continuously moved, agitated, or stirred. This brings all particles into direct contact with the hot gases of combustion and permits the quicksilver vapor to be quickly drawn from the furnace atmosphere. In contrast to the brickwork furnace, ore remains in the furnace only 30 to 90 min., as compared with 6 or 8 hr. up to several days. Nearly complete extraction of the quicksilver from the ore is obtained by roasting the ore above the sublimation temperature of cinnabar and by providing sufficient air to oxidize the sulphur quickly.

Rotary Furnaces.—The rotary furnaces used in quicksilver-ore-reduction plants are of the familiar cement-kiln type. They include a slightly inclined steel shell supported and rotated on two riding rings, or tires, and driven through a pinion by a ring or girth gear fastened to the shell. The riding rings revolve in trunnions and are usually spaced so that the weight of the shell is distributed evenly. The ring gear and drive is usually near the upper ride ring, although this practice is not universal. At each end of the shell, it is necessary to provide gas seals in order to prevent the leakage of quicksilver vapors outward or an inward leakage of cold air. The seals permit the shell to rotate in the stationary hoods at each end of the shell, usually referred to as the firing hood and the dust chamber. The ore is fed to the upper end of the shell by any of several types of feeders, and as the shell rotates the ore rolls and slides downward to be discharged at the lower end.

In usual practice, kilns are counterflow, *i.e.*, the ore is fed in at the upper end and the burner is placed at the lower end so that the gases of combustion and the volatile constituents of the ore travel counter to the flow of the ore and are drawn from the kiln at the upper end. There are, however, a few exceptions, which are later described, in which the kilns are parallel flow. In this arrangement, the ore is fed to the kiln and fired at the upper end and the ore is discharged and the gases withdrawn from the kiln at the lower end.

Rotary-furnace plants are usually rated by the size of the shell, with all other equipment being sized proportionately. The tonnage capacity bears a definite relation to the size of the shell used, although such factors as moisture content of the ore, size and character of the ore, sulphur content (as cinnabar, free sulphur, or other sulphides), and type of fuel used, all influence capacity. One manufacturer[4] lists the following standard sizes, with average range of capacity for each size:

STANDARD SIZES OF ROTARY KILNS

Diameter, in.	Length, ft.	Tons per 24 hr.
21	18	8–12
24	24	12–25
36	40	25–40
36	48	40–60
48	64	60–100
60	84	100–150

There have been kilns of many other sizes built; however, the sizes shown have been accepted as suitable under most circumstances. A typical layout for the 24 in. × 24 ft. size, together with other required equipment, is shown in Fig. 4.

The shells are constructed of rolled steel plate ranging from ¼ in. thickness for the smaller sizes to ½ in. in the largest. Riveted construction is most common, although several all-welded shells have been used.

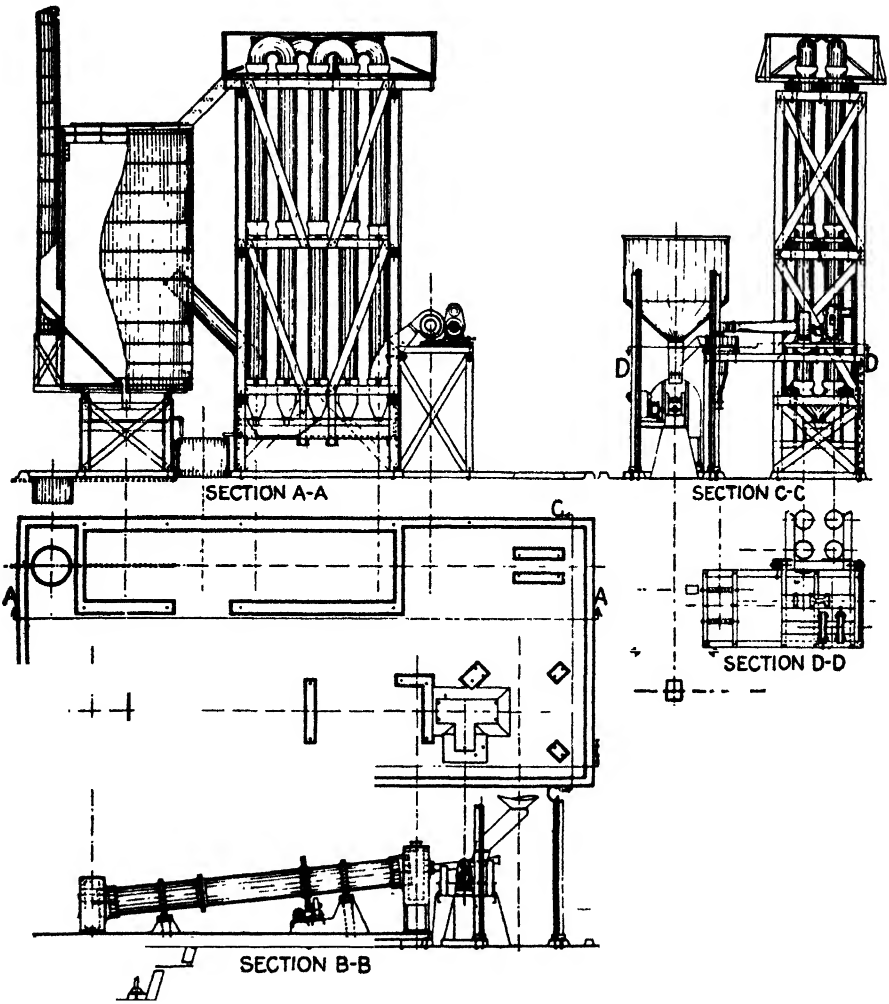

Fig. 4.—Layout of 12- to 25-ton rotary-furnace plant.

In order to protect the shells and as insulation, they are always lined with firebrick or other refractory material. In the standard-size kilns, standard 4½-in. arch brick are usually used, thus giving an inside diameter 9 in. less than the shell diameter listed. Standard 6-in. cupola blocks are used in the 60-in. diameter kilns. Because of the difference in the abrasive nature of various ores, it is difficult to give an average brick-life figure; however, it will probably range from 1 to 5 years of continuous operation. Lining is a relatively inexpensive and simple operation that can be

accomplished in 2 to 5 days, including cooling and starting-up time, depending on the kiln size. In order further to insulate the shell and gain greater fuel economy, most brick linings in rotary kilns are rested on asbestos sheets between the brick and the shell. This material, 1 in. thick and 24 × 36 in. in size, keeps the shell temperature considerably lower and also cushions the brick, thereby prolonging their life.

The inclination of the shell varies from ½ in. per ft. in the largest size to 1¼ in. per ft. in the smallest size. Variations are made not only as to kiln size, but also to assist in adjusting the depth of the bed of ore in the kilns. This is also accomplished by variation of the speed of rotation, which ranges between 30 and 90 sec. per revolution. The kilns are driven by an electric motor, through V-belt drive to a worm or herringbone speed reducer and pinion to the ring gear. Motors installed range from 1 to 7½ hp. with about one-half the installed horsepower being required for operation.

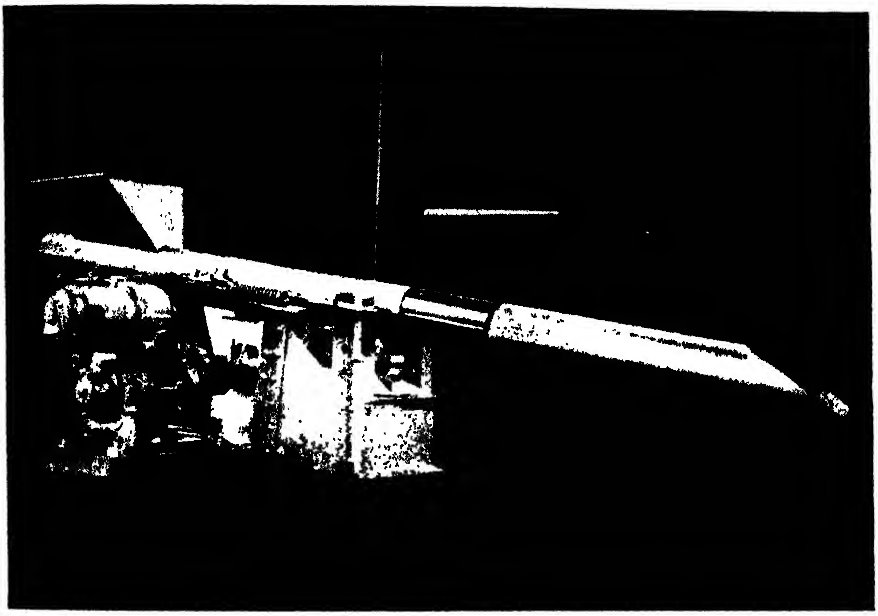

FIG. 5.—Shaker feeder (8-in.).

The seal rings (and expansion joints), located at each end of the shell, are of a number of types. A tight seal is necessary, although pressures seldom exceed ¼ in. of water, in order to prevent fume leakage or an inward leakage of cold air which would tend to condense quicksilver within the kiln or in the flues before reaching the condensing system.

The firing hood, a brick-lined steel hood at the lower end of the kiln, contains the burner equipment and also provides for the disposal of the roasted ore into a bin or hopper below floor level. The dust chamber at the upper end of the kiln derives its name from early practice, when this was a large chamber, usually with baffle walls, in which the gases from the kiln were supposed to drop their dust by reduction in velocity and while still hot enough to prevent condensation of the quicksilver. The development and application of dust-collecting devices have reduced the dust chamber to a small, simple header for the kiln.

Through the dust chamber, the ore is fed into the kiln. The feed to rotary kilns is never sized, and in kilns of the larger sizes, up to 3-in. material can be roasted with satisfactory extraction. The size is largely controlled by the feeder, and for the

smaller-size kilns, material up to 1½ in. is successfully handled. The most satisfactory feeder for handling all types of ore, unsized, wet or dry, is the shaker feeder shown in Fig. 5. The feeder, driven by motor through a variable-speed reducer, has a wide range of capacity and is mechanically simple. The ore is fed into the hopper by gravity, and the feeder tube, ranging from 5 to 10 in. in diameter, resting on rolls or slides, is carried back by the rotation of the cam. At its point of maximum backward travel, it is released by the cam, and springs pull the pipe forward against a bumper block, causing the ore to slide ahead in the pipe and on into the kiln. A range of 30 to 90 r.p.m. of the cam and variable spring tension provide for easy adjustment to various operating requirements. Where the feeder tube extends through the dust chamber into the kiln, a seal must be provided to prevent leakage of fumes. This has been successfully accomplished by using a glass-cloth diaphragm attached to the feeder tube and to the dust chamber. Motors installed for operation of the feeders range from 1 to 7½ hp., and one-fourth to one-third of the installed horsepower is required for operation.

Firing Rotary Furnaces.—Most American rotary-furnace installations have used oil for fuel; however, wood, coal, butane, and natural gas have been used. Butane and natural gas have the advantage of providing a clean fire, easily controlled, but cost usually precludes their use. Coal has not generally been used because of the availability of other fuels and the fact that in order to obtain best results from this fuel the more expensive equipment required for powdered-coal firing is required. Wood has been used successfully at a number of installations where it was available and the transportation of other fuels was costly. It is more difficult to maintain uniform temperature using wood fuel, and the greater volume of gases of combustion reduces the capacity of the plant materially.

Oil firing, consequently, is by far the most popular, and lends itself well to flexibility, ease of control, and economy of operation. Fuels ranging from 12 to 33°Bé. are used, the higher gravity oil usually being used in the smaller plants because of its greater flexibility. It is of prime importance that, whatever fuel is used, good combustion must result in order to prevent the accumulation of soot or tars in the condensing system together with the collected quicksilver. Such soot or tars make the separation of the quicksilver far more difficult, as will be described under Soot Machines.

Oil firing of rotary furnaces has been accomplished in both low-pressure and high-pressure burners, the latter predominating. In either type, the burners are mounted on the firing hood and extend toward or into the lower end of the kiln. In most operations, the lower end of the kiln acts as the combustion chamber; however, some firing hoods have been constructed to contain the mixing chamber, ignition block, and combustion chamber, with only the hot gases of combustion entering the kiln. Considerable progress has been made in recent years in the better design of burner equipment and its application, resulting in better fuel economy. Air is used for atomization, and various schemes have been utilized to preheat the oil and air. The oil is usually preheated in a thermostat-controlled electric oil preheater, whereas the primary and secondary air are most often preheated by the utilization of the waste heat in the burnt-ore bin.

If the high-pressure type of burner is used, air at 40 to 100 lb. per sq. in. must be supplied and requires 3 to 25 hp. through the standard sizes of kilns. Oil is usually (though not always) supplied at similar pressures and requires ¼ to 1 hp.

While the consumption of oil varies in accordance with the character of the ore moisture and sulphur content, size of kiln, and percentage of capacity at which the kiln is being operated, it will range between 4½ and 8 gal. per ton (see later discussion of parallel-flow kilns) and probably average about 6½ gal. per ton.

Although low-pressure burner equipment has been used successfully at a number of installations, it is generally conceded not to be so satisfactory as the high-pressure type when firing a dusty ore. The first cost of low-pressure equipment is equal to or greater than high-pressure equipment, and although power requirements are a little less, oil consumption is usually greater.

Multiple-hearth Furnaces.—Multiple-hearth furnaces consist of a cylindrical metal shell that supports conical or spherical arches of firebrick decked one above the other. A vertical central shaft running through the center of the brick arches carries rabble arms on the various decks, which on rotation rakes the ore across the decks. The feed is at the top, either at the center or on the periphery of the shell, and the ore is raked first outward, then inward, as it drops through ports to the deck below. (The raking action would be reversed depending on whether the feed started at the center or on the periphery.)

The Herreshoff furnace, which is the most commonly used multiple-hearth furnace, is shown in Fig. 6. This furnace is manufactured[5] in a number of standard sizes as follows:

Outside diameter of shell	Number of hearths	Tonnage capacity per 24 hr.
36″ (i.d.)	8	2
10′ 0″	4	20
10′ 0″	6	30
13′ 6″	6	50
16′ 0″	6	75–100
14′ 3″	13	125

The 36-in. size has been successfully used as a laboratory or testing unit and also as a unit for treating concentrates produced by wet-concentration methods. The 13-hearth unit is a new "three-zone furnace" which is described later.

The hollow central shaft is carried on heavy bearings and is rotated by a bevel gear at the bottom, further reduction being obtained by a gear-reduction unit. The speed of rotation of this shaft normally ranges between 45 and 60 sec. per revolution and is determined largely by the period of contact required (or capacity) or the depth of bed of ore on the hearths. The power required is 2 to 3 hp. in the various sizes. The central shaft is hollow in order that cooling air may be blown through an inner pipe, out through the rabble arms, and back into the central shaft outside the inner pipe. The air is either vented at the top of the central shaft or piped back to be used as preheated air in the hearth areas. The power required to provide this cooling air is approximately 3 hp. Notable improvement has been made in the adaptation of heat-resisting metals for the construction of the rabble arms and raking teeth to give them greater life. With adequate air-cooling and design to permit easy access, these items may be changed with very little lost time.

The ore is fed at the top of all furnaces of this type so that the ore must be elevated. This is commonly accomplished through the use of bucket elevators or belt conveyers which discharge into a small surge bin built directly on top of the furnace. From this bin or hopper, the ore drops onto a shelf above the top hearth, from which it is "wiped" off by a feed knife attached to the top rabble arm. The speed of rotation of the central shaft or the pitch of the "wiper" governs the rate of feed.

In order to maintain a uniform bed on each hearth, it is necessary that the ore should be more closely sized than required in rotary-furnace operation; 1¼ in. is

about the maximum size treated. In some of the smaller plants this is reduced to ⅝ or ¾ in.

As the ore travels downward from hearth to hearth, it is thoroughly stirred and exposed to the hot gases of combustion and is finally discharged through a port in the bottom hearth to a burnt-ore hopper under the furnace or directly into a car for tramming away from the furnace.

In the operation of all multiple-hearth furnaces, it is common practice to use one or more of the top hearths for drying or preheating the ore, then dropping onto the next one or more hearths for the roasting of the ore, and finally dropping onto one or more hearths for soaking and cooling before it is finally discharged.

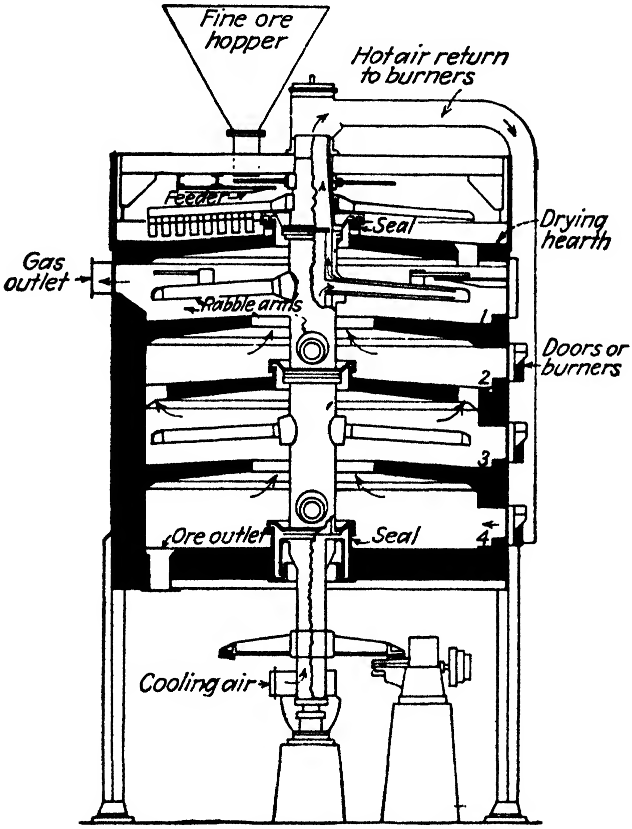

FIG. 6.—Diagrammatic sketch of Herreshoff furnace.

Firing Hearth Furnaces.—Multiple-hearth furnaces, in fields other than quicksilver, have been fired with all fuels; however, as applied to quicksilver, they have, in all but one installation, used oil. The exception used wood at first and finally one-half wood and one-half oil.

Because of the classification of the hearths into drying, roasting, soaking, or cooling zones, the firing is done through ports in the shell on the roasting hearths. In some of the earlier installations, separate fireboxes were built outside the shell; however, because of excessive fuel consumption, all modern installations fire through the shell and directly onto the hearths. Low-pressure burners, using approximately the same range of fuels as are used by the rotary-furnace operations, are used, and oil co

sumption varies because of the same factors that influence oil consumption in rotary furnaces. The average oil consumption, however, is slightly higher, probably approximately 7½ gal. per ton.

Three-zone Hearth Furnace.—A recently installed Herreshoff furnace, described as a "three-zone furnace," is of interest in that an attempt has been made to utilize to as great an extent as possible the waste heat in air used to cool the central shaft and rabble arms and the waste heat from the roasted ore[6]. The furnace is 14 ft. 3 in. in diameter and includes 13 hearths, divided into three zones: the drying zone, consisting

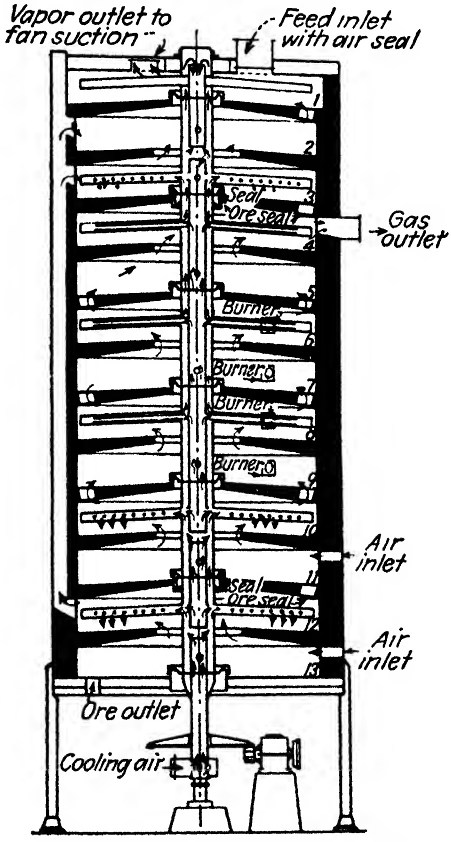

Fig. 7.—Herreshoff three-zone furnace.

of the top three hearths; the central heating zone, consisting of the next eight hearths, the top two being preheat hearths, the next four being burner hearths, and the bottom two being soaking hearths; and the cooling zone, consisting of the two bottom hearths of the furnace.

Figure 7 shows the furnace diagrammatically. Cooling air is forced up the central column and a portion forced out through the rabble arms on the cooling hearths. This portion, together with air admitted through a port in the shell, is drawn off these two hearths through four ducts running to the bottom of the drying zone where it is passed over the wet ore.

Another portion of the central-column cooling air is forced through the rabble arms of the two soaking hearths to combine with additional air admitted through a

port in the shell and provide secondary air for the central heating zone. This air, together with the gases of combustion and volatile products, is drawn off from the top of the central heating zone and sent through a dust collector and condensing system.

Finally, the remainder of the central-column air is forced through the rabble arms of the burner and preheat hearths without escaping to the central-heating-zone atmosphere, and thence through holes in the rabble arms of the top drying zone directly on the ore. In this zone it combines with air preheated in the cooling zone and is drawn from the top of the furnace by a separate exhaust fan and sent to waste.

Substantial fuel savings over the conventional single-zone furnace are reported, and a capacity of 125 tons per day, or more, is obtained.

Because the design of the multiple-hearth furnace requires the installation of a number of brick arches, sprung with a relatively small rise and supported against a circular brick wall within the shell, a variety of brick shapes is required to make a complete lining. Inasmuch as the hearths are largely protected by a bed of ore, there is little abrasive action on the brick by the passage of the ore through the furnace so that brick life, from the standpoint of abrasion, is very good. On the other hand, it is essential that the lining be skillfully and carefully installed to prevent a hearth from sagging or dropping. Likewise, frequent shutdowns and start-ups have a tendency to aggravate this condition and should be avoided.

Comparison of Rotary and Hearth Furnaces.—To compare the rotary furnace with the Herreshoff furnace, it must be realized that in few instances is there an opportunity to make direct comparison on the same type of ore and the same management. At the Bonanza mine in Oregon, the first installation was a Herreshoff, which was followed by two rotary furnaces. After the installation of the rotaries, all ore was screened and the fines roasted in the Herreshoff, the coarse going to the rotaries. The Pinchi Lake mine in British Columbia made an original installation of two rotary furnaces followed by three Wedges. In this operation, likewise, the fines were screened out and fed to the Wedge furnaces. In each of these operations, and it may be generally stated, with proper operation the extraction of quicksilver from the ore may be made equally well in either furnace. Fuel requirements are somewhat higher for the multiple-hearth furnace, and power requirements are possibly slightly higher for the rotary furnace. Although brick wear by abrasion is higher in the rotary, it is doubtful if over-all brick cost is any greater because of the more extensive shutdown required for the occasional repair necessary in the hearth furnace and the more expensive brick required. From the standpoint of general maintenance, the rotary furnace has the advantage. The rotary is simpler to operate and a good deal more flexible than the hearth furnace. Again, in point of initial cost, the rotary has the advantage. It is quite natural, therefore, that rotary-furnace installations have exceeded multiple-hearth-furnace installations by several times.

Flow Sheet of Furnace Plants.—Beyond the furnace, the flow sheets of most quicksilver-ore-reduction plants show a far greater similarity. Notable changes in the equipment beyond the furnace took place about the same time as the development of mechanical furnaces and have been developed with, and because of, the furnace development. This was primarily necessary because of the change of character of the gases evolved from the mechanical furnaces as compared with those of the earlier brickwork furnaces. In the earlier furnaces, many of which operated under natural draft, gas volumes were relatively smaller; because of lack of mechanical agitation of the ore and the smaller gas volumes (and correspondingly, velocity) less dust was carried in the gas stream out of the furnace; a good many of the furnaces predried the ore feed before it entered the furnace (a feature used in part in modern Herreshoff

furnaces), thus reducing water vapor in the condenser gases; and since the development of mechanical furnaces, there has been a substantial reduction in the average grade of ore treated, thus reducing the percentage of mercury vapor in the gas stream.

In the earlier brickwork furnaces, the condensers, therefore, were far simpler—but probably less effective. Dust was not a serious problem and was usually removed from the gas stream by passing the gases through a large brickwork or masonry chamber while they were still hot enough so that the quicksilver would not condense. A reduction in velocity and, at times, baffles, screens, or sprays within this chamber were depended upon to clear the gases of all dust. They then passed into one or several similar chambers, sometimes through a spray of water, for condensation and collection of quicksilver. Although their advantage was simplicity, these condensers had numerous disadvantages: they were more expensive than modern condensers; being built with heavy walls of material of low thermal conductivity, their rate of heat transfer was low and they were necessarily large; the materials of construction would absorb considerable quantities of quicksilver which either would be lost by leakage into the ground beneath them or would be tied up until a portion of this loss could be recovered by "mining" the area under old condensers and the condensers themselves reburned; they presented a difficult cleanup problem in that it was not possible to centralize collection; and they created a very severe health hazard as cleanups frequently meant entry to the chambers for hoeing or flushing out.

The two principal factors, however, that led to improved dust collection and condenser design were the increased amount of dust generated in the mechanical furnaces and the smaller amount of quicksilver in the condenser gases.

Dust Collectors.—Improved dust collection began with the installation of several Cottrell electrical-precipitation units, one on the Herreshoff at the New Almaden mine, and subsequent installations on rotary-furnace plants at the Sulphur Bank mine in California, the Opalite mine in Nevada, and the Arizona Quicksilver Co.'s property in Arizona. At the Sulphur Bank, two Cottrells were installed, one to precipitate the dust, called the "hot-treater," and one to precipitate quicksilver, called the "cold-treater." Although quite effective, their initial cost and high cost of maintenance were excessive and collectors of the familiar cyclone type came into general use.

The use of the first cyclone-type collector at the Knoxville mine in California was followed by its installation at many other plants, and today it is accepted as the most satisfactory unit for either the rotary or multiple-hearth furnace. The more popular type in use is the single-cone type with a fairly large diameter, although several of the multitube type, in which one or more small cones are installed, have been used. Initial cost favors the former, results are about the same, and wear or plugging is against the multitube type.

The quantity and character of dust collected varies over rather wide limits. In quantity it will probably range from as little as ¼ of 1 per cent to over 2½ per cent of the feed. In many plants the operation of the fire or condensing system is given more consideration than the operation of the dust collector; however, they seem to function quite efficiently over a range of volumes and temperatures. Cyclones of the Sirocco type are designed to work most efficiently and at reasonable back pressures when the gas enters at velocities of 1600 to 2000 ft. per min. The gases leaving any quicksilver furnace must be kept above the dewpoint; hence the gases entering the cyclone are relatively hot. The temperature will vary according to furnace design and operation as well as the grade of ore (*i.e.*, concentration of quicksilver vapor in the gas stream); however, it will usually range between 400 and 600°F. In the case of the parallel-flow rotary kilns, later described, the temperature of the gas leaving the kiln is considerably higher.

By employing a properly sized collector with flues of such size that velocities are not excessive and by maintaining temperatures above the dewpoint, the dust collected should be very low in quicksilver content. The loss is attributable to finely divided cinnabar carried out of the furnace by the draft and also to condensed quicksilver. Obviously, the amount of cinnabar depends largely on the character of the mineral in the ore: if the cinnabar is finely crystalline or if the ore is mostly fines, there will be a greater tendency for the cinnabar to be carried over than if it is heavily crystalline or the ore coarse. Condensation of quicksilver in the collector is usually caused by cooling of the gases in "dead pockets" within the collector. It has been found that when ores running 8 lb. per ton or less are being treated, the collected dust approximates the grade of ore being treated. As the grade of ore treated increases, the loss increases somewhat but not in direct proportion. Because the dust collected is a small amount, the total loss of quicksilver, either in quantity or by percentage, is usually small and at most operations is discarded. At several plants, however, flotation, blankets, or hydraulic classification has been employed, with varying results, to recover a part of this loss.

Condensing Systems.—The improvement of the condensing system, as previously stated, was largely influenced by the reduction in grade of ore being treated. Economically, there was the requirement that the maximum recovery should be made—a fact that probably was given less consideration when the more profitable higher grade ores were being treated. Metallurgically, the reduced concentration of quicksilver vapors in the gas stream lowered the dewpoint and required condensers of greater heat-dissipating characteristics than were formerly used. This point has been graphically illustrated by Duschak and Schuette[3]. In attempting to satisfy these two requirements, the other disadvantages of the brickwork condensers were also attacked.

The function of a condensing system is to cool the furnace gases to below the dewpoint, at which condensation begins, and then collect the finely divided globules of condensed quicksilver from the condenser atmosphere and structure. The cooling is primarily essential; the collecting should be as simple and complete as possible.

There has probably not been, since 1917 and 1925, as thorough or comprehensive a study made of quicksilver-furnace gases, their condensation, collection, and losses, as set forth in the *U.S. Bureau of Mines Technical Paper* 96[7] and the *U.S. Bureau of Mines Bulletin* 222[3]. The conclusions reached refer principally to condensation of quicksilver-bearing gases from Scott furnaces and in types of condensers now considered obsolete. It is probably true, however, that much of the subsequent thinking was a direct result of the publication of this information and that directly or indirectly many of the findings were applied to new designs. In fact, however, a direct application of theoretical requirements to the design of a condensing system is impractical, if not impossible. The variation of composition of ores and moisture content, the building up of quicksilver soot on the walls of the condensers, the variation of gas volumes and velocities, changes in atmospheric temperature, pressure, and humidity, and the always variable grade of the ore are some of the factors that would have to be considered in design. As a consequence, and with as many of these factors as possible in mind, condensers were designed, in the builder's opinion, to be adequate for the most demanding conditions of the particular installation. Unfortunately, this opinion was not always sufficient. On the other hand, several types have been designed which proved to be efficient when working within their limits, and sizes have been developed to which the builders are willing to assign a capacity, based largely on averaging the above factors against the ore to be treated. When applied conservatively and with experience and when careful and uniform plant operation is obtained, good results are secured more often than not.

In an attempt to improve the cooling capacity of condensers, it was natural that a break from brick or masonry chambers was the first step. Early installations using metal, glass, wood, and chemical stoneware were tried with varying success; however, they were not generally used until the advent of mechanical furnaces. Soon after their introduction, common vitrified sewer tile was adopted in several different types of layouts. The simplest were no more than long flues, usually leading from a brick or masonry dust chamber to a stack. In size they varied, depending on the volume of gas to be handled, and were often in several strings. This type of system was difficult to clean up and scattered the condensing system over quite a length. The next step was in compacting the tile systems into units, mounted from nearly hori-

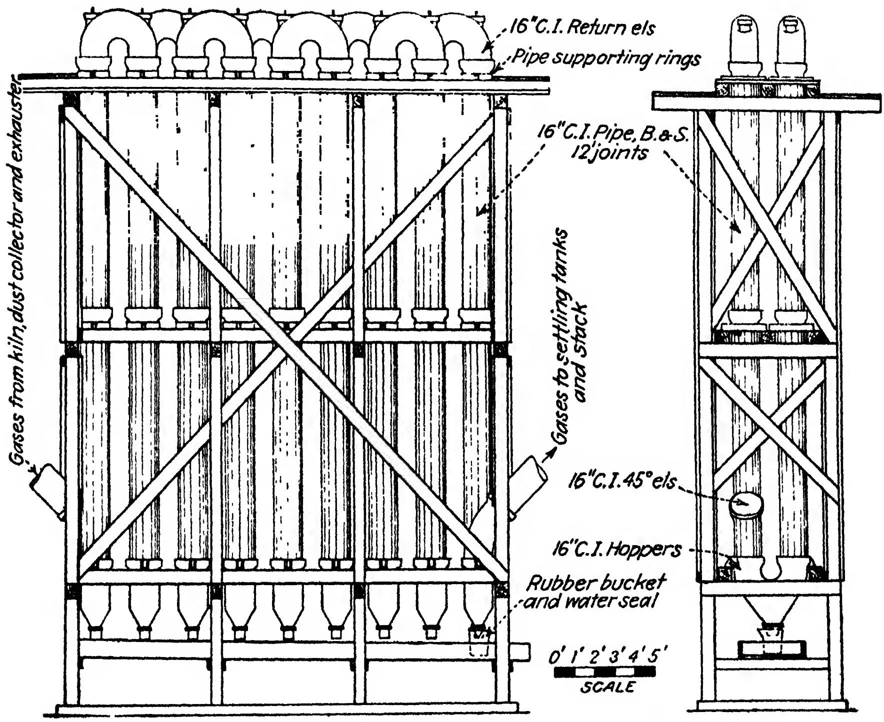

FIG. 8.—Single-row double-deck cast-iron condensing system.

zontal to vertical, by reversing the flow of the gas stream at frequent intervals. A number of different types have been illustrated in *U.S. Bureau of Mines Bulletins* 222 and 335[8]. The most popular European type of condensing system, known as the Cermak condenser, is made of stoneware and consists of pipe joints set vertically with return L's at the top and bottom, the bottom L's having an outlet to facilitate cleanup. The gas travels up and down through the system with frequent reversals of direction.

The tile systems used in this country were far better than the earlier brickwork designs, offering better cooling capacity, centralized cleanup, good baffling action, low cost, and as applied to the industry offered a generally better designed condenser than had been employed theretofore. Tile resists the corrosive action of the sulphurous acid condensed in the system and has a fair resistance to the thermal shock imposed by starting or stopping the operation of a plant or by a spray placed in the system

either for cooling or knocking down dust. In time, however, it has a tendency to crack and require repair.

Metal Condensers.—Although metal condensers had been tried on the brickwork furnaces, after the period of popularity of all-tile condensers (roughly 1917 to 1927), they were again introduced following tile-condenser design (except that pipes were always set vertically). Materials that have since been used, in the order of their popularity, are cast iron, sheet steel, stainless steel, and Monel metal. Each has been used alone, in combination with another, or in combination with tile pipes.

The use of metal pipes immediately draws the criticism of poor resistance to the corrosive effect of the acid condensate within the system. Cast-iron pipe is most commonly used and is probably included in more plants than any other material. One manufacturer uses exclusively a centrifugally cast iron pipe for which is claimed a much better resistance to corrosion than the ordinary cast iron. The pipe used is 16 in. in diameter, has a wall thickness of 0.45 in., and is made in 12-ft. lengths with bell-and-spigot ends. The systems are usually installed as shown in Fig. 8, in stands two lengths high and with specially cast return L's for making the top connection and specially cast hoppers for the bottom connection. In standardizing on a single size of pipe, the system may be sized in accordance with volume and velocity requirements, by length, and by splitting the gas stream into more than one row of pipes.

Although there is a definite relation between area or length or volume contained in the condensing system, it has been many times illustrated that the relation is not in direct ratio to the tonnage being treated. This is probably in part due to variations in excess air required in the different sizes of mechanical furnaces, differences in rate of heat transfer caused by different gas velocities, or differences in composition of furnace gases.

Table 3 shows the make-up of several sizes of cast-iron condensing systems applied to standard rotary furnaces with unit figures based on their maximum capacity in tons of ore treated per day.

The figures cited must be taken as average, as wide variations can exist owing to an extreme condition in one of the variable factors previously mentioned as affecting the design of a condensing system.

TABLE 3.—TYPICAL SIZES OF CAST-IRON CONDENSING SYSTEMS

Type[1]	Tonnage	Pipes[2]	Hoppers[3]	Returns[4]	Total length, ft.	Ft. per ton capacity	Total area, sq. ft.	Sq. ft. per ton capacity	Reversals of direction
SRDD	12	12	4	3	172	14.3	810	67.5	9
SRDD	25	16	5	4	228	9.1	1074	43.0	11
SRDD	40	28	8	7	396	9.9	1865	46.6	17
SRDD	60	32	9	8	452	7.5	2129	35.5	20
DRDD	100	40	12	10	568	5.7	2675	26.8	26
TRDD	150	60	18	15	852	5.7	4013	26.8	39

[1] SRDD indicates a single row of pipes, double decked (2- to 12-ft. joints, 24 ft. high).
DRDD indicates a double row of pipes, double decked (2- to 12-ft. joints, 24 ft. high).
TRDD indicates triple row of pipes, double decked (2- to 12-ft. joints, 24 ft. high).

[2] Pipes are cast iron, 16 in. i.d., 12 ft. long, 0.45 in. wall thickness, bell-and-spigot ends.

[3] Hoppers are cast iron, 16 in. i.d., return L's, but with an outlet at the bottom for water seal and cleaning.

[4] Returns are cast iron, 16 in. i.d., return L's, but with a cleanout hole over each outlet for cleaning of pipes.

In operation cast-iron condensing systems are simple and efficient. They operate at input temperatures varying from 450 to 250°F., and outlet temperatures of 100 to 160°F. Because a coating of quicksilver soot builds up on the walls of the pipes, they are periodically washed down at intervals ranging from 24 hr. to 14 days. The frequency depends on the amount of dust escaping the dust collector, the quantity of sulphur reprecipitated, the accumulation of soot or tars caused by imperfect combustion in the furnace, the amount of moisture and quicksilver in the ore, and occasionally on a routine requirement for shutdown for servicing power plant or other equipment. In multiple-row systems, dampers are occasionally installed so that one row may be washed down without necessitating a cessation of furnacing. The time required for washdown varies from about 30 min. to 2 hr. In the washing-down operation, a hose with a spray attachment is dropped into each stand of pipe through the cleanout holes in the returns. The soot, or mud, drops to the hoppers where it is caught in buckets under each hopper spout. The buckets are removed, emptied, and replaced for further operation. Between washdowns, there is a certain amount of "drop-down" which is collected daily or oftener if required. The ratio of material collected in the drop-down to that collected in the washdown varies considerably. In most instances the higher the sulphur content in the ore, the greater the hang-up, although on the average, the amount collected in the washdown approximately equals the total collected by daily drop-down. The buckets collect the drop-down continuously by maintaining a water seal over the hopper spout. The buckets used are usually hard rubber to resist the corrosive action of the water.

The cast-iron pipes, hoppers, and returns, though attacked by the sulphurous solutions, vary in life depending mostly on the sulphur content of the ore being treated. In the hot end of the condensing system and before the dewpoint of the water vapor is reached, they will last almost indefinitely. As the gas stream becomes wet, the metal is attacked, and in this portion of the system, the life varies from 1 to 5 years. Despite the requirement for replacement, but because of their low initial cost, the ease of installation, and their high rate of heat transfer, they are the most popular type in operation.

Sheet-steel condensers, of welded construction, designed to the same layout as the cast-iron system, have been installed in several reduction plants. They have been built of material ranging from 18 gage to ¼ in. thickness. Their resistance to corrosive attack is less than that of cast iron, and the lightweight material used only justifies their installation for the treatment of very low sulphur ores. They have been particularly popular in Nevada installations whose ores are most often of this type. Although they have a somewhat higher rate of heat transfer than cast-iron pipes, they are usually constructed in about the same sizes.

There were a few Monel-metal systems built, ranging in weight of material from 24 to 28 gauge; however, their performance did not justify the original cost.

Stainless steel, type 317, has been included in a combination system at Nevada property, together with sheet iron and cast iron. The system is made up of a large number of 9-in.-diameter pipes, 12-gauge black iron being used in the hot end of the system, cast iron being used in the middle, and stainless steel at the cold end. The resistance of the stainless to sulphurous attack is good; however, the occurrence of occasional chlorides in this ore adds a corrosive constituent to this gas not found elsewhere, and one that attacks the stainless-steel pipes.

Several installations have economically and efficiently combined sheet steel with cast iron and sheet steel with tile, in either case the sheet steel being installed on the hot end.

Several methods have been used for connecting the pipes at the top and the bottom of the stands; however, the most commonly used is a cast-iron or fabricated-steel

return L. Next in popularity is the use of tile Y branches, the straight section being set on a 45-deg. slope with the branch pointed vertically upward. Several Y branches may be joined to form a common base for several stands of pipe. The bottom end of the branch line is often submersed in a tank of water to provide a water seal and prevent leakage during cleanup.

The top connections are possibly more varied as to detail but usually simulate the return L, the Y branch, or a T, with or without cleanout openings.

It will be noted that in attempting to improve the cooling capacity of condensing systems, which ultimately resulted in largely swinging to metal condensers, the other objectionable features of earlier systems have also been improved. Costs, as shown later, are lower. The almost complete elimination of sprays, at least inside the system, has been advisable for several reasons: the satisfactory application of dust collectors has lessened their requirement for knocking down the dust; there is less water overflow from the condensers reducing water losses; the cooling efficiency of water in the system is poor; and the spray of water on a metal pipe hastens its failure by corrosion. Water sprays are sometimes applied to the outside of metal systems, although this is usually done to make effective an undersized system, to increase the capacity of a system, or to combat excessive summer atmospheric temperatures. Modern systems have been compacted so that cleanup can be made in a relatively small area and mechanical losses thereby reduced. The reduction in the health hazard has been one of the more important accomplishments of new systems. Leakage has been reduced to a minimum by making the condensers of an impervious material which upon the first break-through is easily detected and repaired; the method of cleanup exposes workmen to a minimum of quicksilver fumes; and, because of their simplicity and compactness, there is less quicksilver tied up to contaminate the atmosphere around a quicksilver plant.

Exhaust Fans.—Discussion of exhaust fans has been given ahead of description of the condensers as there are three locations—for either rotary or Herreshoff furnace installations—in which they have been placed.

The location determines the physical requirements necessary in the exhauster, although it is doubtful that there is any material metallurgical advantage in one location over another.

Many of the older brickwork plants used exhausters for maintaining a draft over the firebox, and these exhausters were nearly always located at the end of the condensing system or at the base of the stack. They operated in a wet and corrosive atmosphere at temperatures probably ranging from 90 to 140°F., and were commonly made all, or in part, of wood to resist corrosive attack.

In modern mechanical furnaces they have been placed (1) between the furnace and the dust collector, (2) between the dust collector and the condensers, and (3) between the condensers and the settling tanks or stack.

Although there were a number of installations made as in 1, the temperature of the gases at this point gave rise to operating difficulties in bearing wear and abrasive attack by the dust-laden gases. This was partly overcome by the use of water-cooled bearings, but these did not prove entirely satisfactory.

The bulk of installations are as in 2. At this point, gas temperatures are seldom over 400°F., and improvement in ball-bearing design and the inclusion of heat-reflecting plates and fans on the exhauster shaft make modern exhausters entirely satisfactory in this temperature range. By placing the exhauster after the dust collector, abrasive action of the dust is nearly eliminated and the gases are still hot enough to be dry and therefore noncorrosive.

The installation of the exhauster at the end of the condensing system has become more popular with the development of acid-resistant exhausters. The old wood-

scroll and wood-impeller designs are unsatisfactory; however, corrosion-resistant metals or rubber-coated exhausters are quite satisfactory. The latter are more commonly used and, barring accident to the coating, are useful for a long life.

It may be argued in favor of location 2 that (*a*) there is no corrosive attack by wet gases, (*b*) better dust-collector action and draft control is gained, and (*c*) any leakage in the condensers is immediately discernible and can be repaired. In favor of location 3, (*a*) severe bearing wear is eliminated, (*b*) a smaller volume of gases is handled because of the lower temperature, and (*c*) the condenser system is always under a negative pressure, thereby preventing leakage of fumes. There is probably little to choose by except individual preference and the somewhat higher cost of the rubber-coated fan.

All modern installations use electrically-driven exhausters, many of which are equipped with variable-speed drives in order to make adjustments easily and quickly to control draft properly under variable conditions. The power required varies from about 1 hp. at 10 tons daily capacity to 10 hp. at 150 tons per day.

Settling Tanks.—The utilization of settling tanks beyond the condensing system has become standard practice on most mechanical-furnace installations. Their function as a cooler in the condensing system is all but precluded by the fact that the gases at this point are wet and corrosive and that to be effective as a settling tank they must be large, so cannot be economically built of material with a high rate of heat transfer. As a consequence, they are commonly built of wood. Tanks have ranged from 5 to 24 ft. in diameter and 6 to 20 ft. in height, and may be installed singly or in number. In a commonly used tank, the staves are 20 ft. in length and the tank is 10 ft. in diameter and is supported by $\frac{5}{8}$-in. steel-rod hoops. A conical redwood bottom facilitates cleanup. Entry, from the condensing system, is usually made by cutting a hole in the side of the tank, so that the entry pipe can be inserted on an upward angle anywhere above the cone. The exit pipe is similarly cut in just above the cone and may lead to another tank, or stack line, or the stack may be mounted on the side of the tank. Connection pipes are usually made of wood-stave pipe or tile.

Although these tanks are poor coolers, they do provide a settling area in which final traces of uncollected quicksilver may be collected. The reduction in velocity, plus the baffling effect gained by the eddying of the gas stream within the tank, assists in collecting the minute globules that may have carried through the condensing system attached to a particle of dust or droplet of water. In some installations, baffles or sprays have been added to the tanks.

The use of settling tanks adds a safety factor to the operation of all plants in standing by as additional collector in the event of misoperation of other units within the plant. Likewise, it provides a measure of over-all operation in that, if more than the usual amount of quicksilver is collected from the tanks, the condensing system, tonnage, and draft should be checked for changes from normal operational procedure. The normal amount collected, as in the condensing system, varies according to several factors; however, the tank system should not collect more than 1 per cent of the total quicksilver collected. If it exceeds this amount, stack losses may be excessive.

Stack Lines and Stack.—Beyond the tank system, the condensation and collection of quicksilver should have been essentially completed. The stack, therefore, is primarily to convey the gases of combustion, water vapor, sulphur dioxide, and other gases away from the plant for waste. The importance of a stack line, *i.e.*, the line from the tank system to the base of the stack, has largely declined with the universal application of exhaust fans to provide draft control. There are some, however, who continue to advocate their use, although it would seem that their only advantage

would be as an additional collecting facility or to raise the stack to such an elevation that power requirements on the exhaust fan are reduced. Modern plants are, therefore, about equally divided between those using a stack line and those which mount a stack on or alongside the final tank. Stack lines, likewise, are about equally divided between tile and wood construction, whereas stacks are almost entirely of wooden construction. Redwood is the commonly used wood in the construction of tanks, connection pipes, and stacks, although fir has been used. It withstands the action of the acid quite well, and the life of these units will probably average 5 to 10 years. The temperature of the gas at the stack should not exceed 140°F., lest high stack losses be encouraged. They will run down to relatively low temperatures depending upon the atmospheric temperature.

Soot Machines.—Soot machines have been developed to handle the product of the condensing system, commonly referred to as "soot" or "mud," although in most of the older plants, and even up to quite recently, it was worked by hand. Soot includes dust that escaped the dust collector and was knocked down in the condensers, unoxidized sulphur precipitated out of the gas stream, residues from unburned fuel, precipitates from other volatile constituents of the ore (As, Sb, etc.), water and quicksilver. It is collected in buckets or launders under the condensers, settling tanks, and from the stack line and stack. The quantity varies greatly, as previously shown, as does the percentage of the constituents.

Older practice consisted of decanting the water from soot, mixing in unslaked lime to dry it and make the finely divided (floured) quicksilver coalesce into large globules, and hoeing. The soot was placed on an iron table varying in size from 12 to 50 sq. ft. with 4-in. sides and set with a slope to one corner. It was then manually hoed (mixed and raked) across the table, and the separated quicksilver flowed to the low corner, from which it overflowed through a gooseneck to a storage pot.

Under the table, steam or hot-water pipes and not uncommonly a wood fire assisted in drying the soot and facilitated the separation. The quicksilver fumes escaping from the table, though probably not so large as to constitute a serious loss of quicksilver, contaminate the surrounding atmosphere with a concentration sufficiently high to be dangerous to the workmen. Various ventilating systems have proved only partially successful.

Because of this hazard, the cost of labor, and the fact that a sometimes rather low recovery is made by hand-hoeing, numerous mechanical devices have been devised.

The most widely used is a circular pan, 3 to 6 ft. in diameter, with a vertical central shaft to carry mixing and stirring paddles. The soot and lime are placed in the pan and hoed by the rotation of the paddles either for a predetermined period or until the soot is impoverished of the bulk of the quicksilver. For best operation, the paddles rotate at 5 to 10 r.p.m., and the pan is set on an inclination of about 1½ in. per ft. A slot at the low point of the pan, connected with a gooseneck, creates a puddle which assists in the collection of the finely divided quicksilver. The pan may or may not be equipped with a heating device, although a hot-water compartment, kept at 150 to 160°F., materially improves results. The top of the machine may be tightly enclosed, thereby preventing fume leakage. When driven through a worm reducer, the power required ranges from 1 to 5 hp.

Many other devices have been used, some with good success, but the above type is most commonly used. Other types include agitators (both wet and dry), centrifuge types, presses, screw classifiers, and probably many others.

In most instances the hoed soot is returned to the furnace feed so that the unreclaimed quicksilver in the soot is ultimately recovered. At some plants a retort is kept in operation for the treatment of the hoed soot on the basis that returning the soot to the furnace only increases the dust problem. Because the soot collected

seldom exceeds 10 per cent of the dust collected, this does not seem important, and at several operations tests showed that dust conditions were no less favorable when the dust was returned to the furnace.

Auxiliary Equipment.—Additional equipment required in the modern furnace plant is not extensive and includes that common in other milling plants, such as bins, crusher, screens, conveying or elevating equipment, and a power plant.

Bins required are for coarse and fine ore and for burnt ore. Many of the new plants have utilized steel bins for fine ore and burnt ore but have kept wood bins for coarse-ore storage. The result is larger coarse-ore storage and a reduction in fire hazard in the main plant. Many concrete burnt-ore bins are in use, and although they have a tendency to crack from the heat, their usually small size (10 to 75 tons capacity) does not make this serious.

The crushing of quicksilver ores is perhaps less difficult than that of many others. Except for the opalite and rhyolite ores of Nevada and Oregon, a few hard limestone ores, and still fewer hard serpentine ores, most quicksilver occurs in sandstones or shales that are relatively easy to crush. In preparation for rotary furnaces, the ore does not have to be reduced to less than 2 to 3 in., which can be accomplished in a single pass through a jaw crusher. Inasmuch as hearth furnaces require a smaller size of feed, installations for plants of this type usually include a jaw crusher in closed circuit with a shaking screen and necessary conveyer or elevators. Because the greatest number of quicksilver plants fall within the range of 20 to 75 tons daily capacity, jaw crushers commonly range from 6 × 8 in. to 10 × 20 in. in size and are mostly of the Universal or Blake type. Screens, where used, are of the shaker type and are sized according to the hearth-furnace requirements.

Conveyers or bucket elevators, because of the usually small capacity required and because plants are relatively compact, are not extensive.

TABLE 4.—INSTALLED HORSEPOWER REQUIREMENTS FOR ROTARY-FURNACE PLANT INSTALLATIONS

	Daily plant capacity, tons					
	8–12	12–25	25–40	40–60	60–100	100–150
1. Kiln	1	2	3	3	5	7½
2. Feeder	1	2	3	3	5	7½
3. Exhaust fan	1	2	3	5	7½	10
4. Compressor for oil firing	3	5	7½	10	15	25
5. Oil pump	¼	¼	½	½	¾	1
6. Oil preheater	¾	1¼	2	2½	3¼	4
7. Crusher	5	7½	10	15	20	25
8. Conveyer	1	2	3	3	5	7½
9. Lights and miscellaneous	2	2	3	3	5	10
10. Total horsepower installed	15	24	35	45	66½	97½
11. Usually installed generator, kw.	15	20	30	40	50	75

Items 4, 6, 7 8, and 9 are at average conditions.

The power requirements for all quicksilver-reduction plants are relatively small. Although the number of plants that are served by power companies are increasing, the majority of plants have to generate their own. The power consumed in the early plants, as already stated, was little and was usually steam. This was replaced with

the development of the oil engine, and up to the First World War most plants were line-shaft driven. Since that time, however, the improvement of diesel engines has been responsible for their greater application together with alternating-current generators. This has made possible individual electric drives on each piece of equipment with attendant greater flexibility and efficiency.

The installed horsepower requirements of rotary-furnace installations, together with the usually installed size of diesel-generator plant, are shown in Table 4. Requirements for compressor and oil preheater are subject to change for altitude and climate conditions; for the crusher depending on type of ore; and for conveyer and lights and miscellaneous, on topographic, camp, layout, and other factors.

Actual power consumption will be approximately one-half the installed horsepower when the plant is operating continuously.

Control of Operations and Assaying.—Quicksilver-plant operators largely depend on the manufacturer to provide a furnace designed to operate efficiently within a certain tonnage range on a particular type of ore. As a consequence, it is up to the manufacturer, based on an estimation of the various factors previously described, and experience, to provide a plant meeting the tonnage specifications. Tangible and intangible factors are, therefore, considered in such design, and after installation is made certain tests can be performed to set up operating conditions at various tonnages. Likewise, such tests should be performed when changes of ore occur, as in character, grade, and moisture and sulphur content, or when equipment or other related conditions are changed.

The tests consist of making an accurate determination of the weight of the ore being treated and its moisture content; the grade of ore must be determined; the fuel consumption must be measured; a determination of the CO_2 content in the furnace gases must be made; and pressure and temperature readings must be taken throughout the plant. With the results of these tests in hand and as described in more detail in *U.S. Bureau of Mines Bulletin* 335[8], it is possible to adopt operating conditions within safe limits.

In practice it is common to measure ore by occasionally weighing a cubic foot and then assigning weights to cars, trucks, or other means employed to transport the ore into or away from the plant. Few plants weigh automatically or continuously. Likewise, occasional checks are made on moisture content and grade of ore. The difficulty in sampling of quicksilver ores due to the erratic occurrence of the cinnabar in the ore and its friability and tendency to concentrate in the fines increases the difficulty of checking metallurgical operation; however, if carried out carefully and with due recognition of the factors involved, sampling will give good results. Assaying the samples is usually performed in the Whitton apparatus or by the so-called Bureau of Mines method[9], the latter being preferred because of its greater accuracy and because assays may be made more quickly.

In the Whitton method, the ore sample, together with fluxes, is placed in a metal retort tube closed at one end. A clean, weighed gold or silver foil is placed over the open end and a metal cup clamped down on it, sealing the retort. The cup is filled with water, and as the retort is heated, the quicksilver vapor rises in the retort to the foil, on which it condenses and amalgamates. The foil is again weighed, the increase showing the amount of quicksilver in the sample.

The Bureau of Mines method, described in detail in *Technical Paper* 227, consists of volatilizing the quicksilver in a sample, in a test tube, and collecting the quicksilver on the cold upper walls of the same test tube. After complete volatilization of the quicksilver, the lower half of the test tube, including the burnt sample, is broken off and discarded. The upper half including the condensed quicksilver is washed with nitric acid in a beaker, potassium permanganate added to this solution until it

remains colored, and peroxide added until the color disappears. With ferric sulphate as an indicator, the solution is then titrated with potassium thiocyanate. This method is simple and can easily be used in plant control work for checking head samples and also burnt-ore samples.

Fuel consumption is measured either by meter or by gauging fuel tanks and for the purpose of test periods can be measured quite accurately.

Determination of the CO_2 content of the furnace gases should be made in order to determine the total gas volume and the amount of excess air drawn through the furnace. From the former it is possible to calculate stack losses, and from the latter a measure of the thermal efficiency of the plant is gained. These determinations need not be made at frequent intervals after operating conditions are established.

The use of a draft gauge to measure pressures throughout the system and a thermometer to check temperatures at frequent intervals are the two most practical applications to control of operations. If it is assumed that, after a general checking of one plant, operating conditions have been established within certain ranges, the draft gauge and the thermometer give a relative indication of all conditions. As a consequence, these are the only instruments generally relied on for indicating or recording, continuously, conditions affecting control. Thermometers are usually installed to measure temperature of the gas stream somewhere between the furnace and the condensers, and occasionally at the end of the condensers and at the stack. Draft gauges are usually installed on the furnace at the gas outlet and occasionally in the condensers or at the stack. A manometer is often installed at the fan to measure the back pressure of the dust collector. The usefulness of draft gauges is their ability to measure changes in pressure in the system caused by leakage or by plugging so that proper steps may be taken to alleviate the trouble.

For the most part, quicksilver plants operate with very little control apparatus after they have once been adjusted and regulated. Occasional check tests are very desirable, but normal operation is usually left to the operator, who, by observation, can quite easily detect changes in conditions as they develop. Because simple regulation to offset these changes is possible, automatic control devices are not usually justified.

Losses.—Losses in quicksilver-reduction plants may occur at the following points: (1) in the burnt ore, (2) in the dust, (3) through the stack, (4) by solution or mechanically in water overflow, (5) by spillage and through handling.

Losses in the burnt ore are primarily a function of the temperature at which the rock is burned and the period it remains at or near that temperature. In most operations the burnt-ore loss can be considered as very small, although on low-grade ores the economy of striving for complete extraction is sometimes offset by fuel cost versus increased furnace capacity and greater gross production. It is difficult to establish the point at which one offsets the other, owing to the differences in burning characteristics of different types of ore, cost of fuel oil, and the price obtained for the quicksilver produced. In properly operated furnaces, however, and on average grade ores, the burned rock may show average assays of 0.02 to 0.05 lb. per ton. Many operations checked show lower values than these, and of course, there are some that run higher.

Dust losses have been discussed and the amount shown to be, on average ores (ores averaging less than 8 lb. per ton), approximately equal in grade to the grade of the ore. If the dust collected represents ¼ of 1 per cent to 2½ per cent of the ore feed, these figures would represent the loss in the dust if no attempt was made to recover any of the values from it.

Stack losses have probably been blamed in more instances than anything else for the failure of a plant to recover quicksilver from the ore; however, most operators as well

as many others have used a variety of procedures to determine their exact amount. The more reliable tests show that they are nearly always small, and there is little reason to believe that, with a condensing system properly designed and operated, losses could represent more than 1 per cent. The best evidence of low stack loss is that, if it was as high as has been suspected, it would coat the surrounding area with quicksilver in a short period, thus advertising such a loss. When periodic cleanups of the stackline and stack do not recover much quicksilver, there are not high stack losses.

Quicksilver lost either mechanically or by solution in overflow water from the condensers should be nearly negligible. All overflow water should be collected in launders and run to settling boxes arranged with baffles to cause the current to underflow. This will collect most of the mechanically transported metal; the metal in solution could not be economically recovered.

Spillage and handling losses are a matter of good housekeeping and supervision. Concrete floors in the areas under the condensers, with drains to the launders leading to the settling boxes, should always be laid and kept in good repair. Smooth surfaces and the filling of any cracks that might develop make it possible to clean up the area and recover any quicksilver that may have been spilled. The development of a careful operating routine will also assist in avoiding losses of this type.

In general, it may be stated that all losses in a well-designed and -operated plant should not exceed 5 per cent, and under certain conditions and with devices to assist in the recovery of dust, water, and spillage, losses may be reduced to as little as 1 or 2 per cent.

Cost of Furnace Plants.—It is difficult to compare furnace-plant costs in different years due to economic conditions, relative value of the dollar, differences as to extent of equipment included, and differences in the cost of installation due to location. It is interesting, however, to note that the range \$500 to \$1000 per ton of daily capacity has been used since the earliest American plants were built and is still a good figure. By virtue of the decreased value of the dollar, however, this would indicate that modern plants are actually less expensive. Egleston[10] reports the cost of the two modified New Idria type furnaces at the Redington mine in California as between \$100,000 and \$125,000, built about 1868, and the cost of Knox-Osborn furnaces as between \$14,000 and \$9000 in 1874. Inasmuch as the capacity of the modified New Idria type furnaces was about 30 tons per day and the Knox-Osborn furnaces 24 and 12 tons per day, their cost per ton of daily capacity was, roughly, \$2100, \$600, and \$750, respectively. It is quite likely, however, that the cost of the Redington plant may have included more than just furnace-plant equipment.

Scott furnace plants, since their inception, have been figured at \$400 to \$1000 per ton depending on capacity, location, and the times. In 1917, Bradley[11] stated their cost, though influenced by wartime prices, would approximate \$1000 per ton of daily capacity, although he recognized that they had been built at lower costs.

Mechanical furnaces at approximately the same time were estimated at between \$600 and \$1500 per ton of capacity; however, improvements in their design and operation have gradually increased their capacity, thus lowering per ton costs. All things considered, the hearth-type furnaces are slightly higher in cost than rotary-furnace-plant installations. The quoted prices and estimates of several common sizes of rotary-furnace plants by one manufacturer[4] as of July, 1941, are shown in Table 5 Because of wartime inflation, these costs are approximately 15 per cent above average prices for the period 1935–1939.

Although installation costs have been estimated, they are approximately the average of a number of plants of each size built at that time. These costs include all engineering costs, and the installation cost includes the services of an operator for 30

days after completion of the installation to train the operating crew, make tests, and develop the operating routine.

TABLE 5.—APPROXIMATE COSTS OF ROTARY PLANTS, JULY, 1941

	21″ × 18′ 8–12 tons	24″ × 24′ 12–25 tons	36″ × 48′ 40–60 tons	48″ × 64′ 60–100 tons
Kiln, including shell, ride and drive mechanism, seal rings, speed reducer, frame, hoods and shaker feeder	$ 3,025	$ 3 910	$ 6,889	$10,180
Oil-firing equipment, including compressor, receiver, oil pump, gauges, meter, strainer, preheater, and 2 complete burners	679	982	1,089	1,315
Dust-collecting equipment, including collector, exhauster receptacle, and connections	478	596	785	1,045
Condensing system, including cast-iron hoppers, pipes and returns, redwood tanks and stack, recording thermometer, connections and condensing-system auxiliaries	2,030	2,655	4,325	6,415
Motors and drives, including kiln, feeder, compressor, oil pump, and exhauster	868	847	1,038	1,325
Power unit, including caterpillar diesel-generator unit with fuel-transfer tank, switchboard with motor switch gear, and lights transformer	2,317	2,699	3,519	4,719
Brick, including lining for kiln and firing hood	80	154	422	753
Fuel-oil-storage tank, bolted-steel construction	275	378	526	545
Steel fine-ore bin	620	673	1,028	1,350
Steel burnt-ore bin	335	706	1,082	1,095
Crusher, including cast-steel jaw crusher, motor, starter and drive	1,108	1,180	1,383	1,873
Total cost of equipment, f.o.b. San Francisco	$11,815	$14,780	$22,095	$30,615
Estimated cost of freight, excavation, and installation, including all concrete work, coarse-ore bin, conveyer, frame and corrugated-iron building, and piping and wiring	5,000	6,750	8,750	12,250
Estimated total cost of installed plant	$16,815	$21,530	$30,845	$42,865
Cost per ton capacity, installed at average of tonnage rating	$ 1,682	$ 1,164	$ 617	$ 536

Operating Costs.—Operating costs, even as the cost of the furnace plants, are largely predicated on the times and vary with the price of labor and the price of fuel ., the two principal items of cost. Table 6 shows a hypothetical estimate of costs

of rotary-furnace-plant operations based on 1944 and 1941 conditions. Actually, costs for the period 1935–1939 would approximate 20 to 30 per cent lower than the 1941 figures.

TABLE 6.—ESTIMATED COST OF OPERATION OF ROTARY-FURNACE PLANTS, 1941 AND 1944

	Average of daily rated capacity, tons per 24 hr.					
	10	$18\frac{1}{2}$	$32\frac{1}{2}$	50	80	125
Firemen, number required	3	3	3	3	3	3
Cleanup men, number required	....	....	1	1	1	2
Foremen, number required	....	....	....	....	1	1
Labor cost per ton, 1944	2.85	1.54	1.17	0.76	0.63	0.48
Labor cost per ton, 1941	1.80	0.92	0 74	0.48	0 43	0 32
Oil consumption, gallons per ton	$7\frac{1}{2}$	7	$6\frac{1}{2}$	6	$5\frac{1}{2}$	5
Oil cost, per ton	0.64	0.60	0.42	0.39	0.36	0.33
Supplies, repairs, power and maintenance, per ton	0.60	0.50	0.40	0.35	0.30	0 20
Total operating cost, per ton, 1944	4.09	2 64	1 99	1 50	1 29	1 10
Total operating cost, per ton, 1941	3.04	2.02	1.56	1.22	1.09	0 85

Although these figures are based on hypothetical requirements, they approximate actual costs for the two periods mentioned. Labor costs for firemen and cleanup men are based on \$9.50 per day, average daily wage (7 days per week, including 1 day at time and one-half and 1 day at double time), including compensation insurance, social security, and unemployment insurance, for 1944, and \$6 per day for 1941. Foremen are bracketed at \$12 per day in 1944 and \$10 per day in 1941, being the average daily rates over a monthly period.

The variation in oil consumption is purely hypothetical, although it may be stated as average figures. A difference of 2 cents per gallon is allowed on the cost of fuel oil for the two smaller sized plants, their fuel being figured at an average of $8\frac{1}{2}$ cents per gallon, whereas the larger kilns are assumed to use heavy oil at $6\frac{1}{2}$ cents per gallon.

Supplies, repairs, power, and maintenance are estimated, in a liberal amount, to cover these items. Supplies include only lime for hoeing. Repairs and maintenance are generous enough to provide, over a period of 2 or 3 years' operation, for all charges. Power is figured at an average for purchased or locally generated power, including repairs to power plant if locally generated.

While these figures are estimated as average figures for rotary-furnace operations, there may be substitutial variations in either direction depending on ore characteristics and local conditions, although they may be used for estimating purposes. The sometimes lower quoted costs of Scott or other brickwork-furnace operations, and even other rotary- or hearth-furnace operations, if translated to present conditions, variations in ore being treated, or other operational factors, would approximate the figures of Table 6.

Description of Plants. *New Idria Mine, California.*—Figure 9 shows the flow sheet of the New Idria plant. Furnace equipment consists of four 5 × 6 ft. rotaries built in 1917. They have recently been rebuilt and the complete plant modernized. The burnt-ore bins are concrete. The kilns are fired with 16 to 18°Bé. fuel oil in National Aerol burners. Air pressure is 90 lb. per sq. in. and oil pressure 28 lb. per

sq. in. The firing hoods are so designed as to mix the air and oil in a mixing chamber and fire through a combustion block, all set outside the kiln, in order to gain as great an effective length in the kilns as possible. Shaker feeders feed an average of 100 tons per day to kilns 1 and 2, and 120 tons per day to kilns 3 and 4. Gases are drawn from each kiln by American Blower Co. No. 35 exhausters through No. 12 Sirocco dust collectors. The condensing systems on kilns 1 and 2 include forty 16 in. × 12 ft. cast-iron pipes with 12 hoppers and 10 returns; on kilns 3 and 4 each system includes 60 pipes of the same size and 18 hoppers and 15 returns. Numbers 1 and 2 are double-row double-deck systems, and Nos. 3 and 4 are triple-row double-deck systems. The

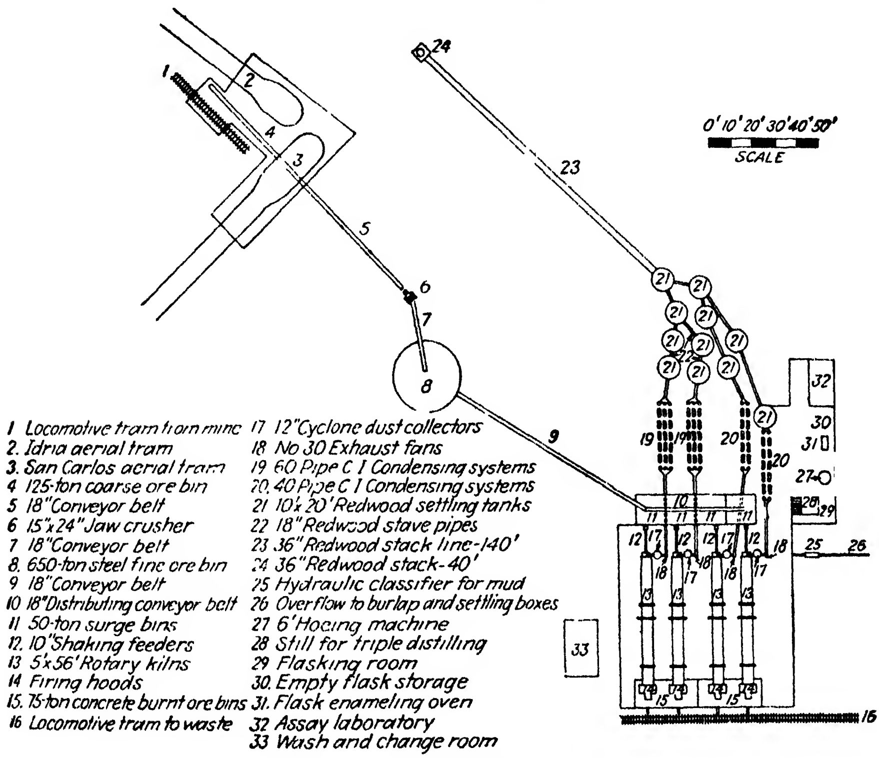

FIG. 9.—New Idria flow sheet.

tank system, as illustrated, is made up of 10-ft. diameter by 20 ft. high redwood tanks with 2-in. staves. The stack line consists of a 36-in. redwood continuous pipe to a concrete stack base supporting a 36-in. redwood stack 40 ft. high. It will be noted that each kiln and condensing system is kept separate until the middle of the tank system is reached. Dust is removed continuously from the collectors hydraulically and is combined with all condenser-system overflow water and all spillage on the floor and run through a specially designed hydraulic classifier. All soot is mechanically hoed and the soot returned to the furnaces. The quicksilver, after leaving the soot machine, is washed and flows directly into storage tanks, from which it is drawn for flasking. All flasking is done through a volumetric weighing device to ensure accurate measure. Ore is transported from the mine by two aerial tramways and by electric haulage to a tramway terminal bin of 125 tons capacity. From this bin it is conveyed to a 15 × 24 in. jaw crusher, all being reduced to minus 3 in. A second con-

veyer moves the crushed ore to a 650-ton steel fine-ore bin. A third conveyer draws from this bin and feeds a shuttle conveyer over the top of four furnace surge bins of approximately 50 tons capacity each. The ore feeds by gravity from these surge bins into the shaker feeders. The mine is served by a 55-mile power line.

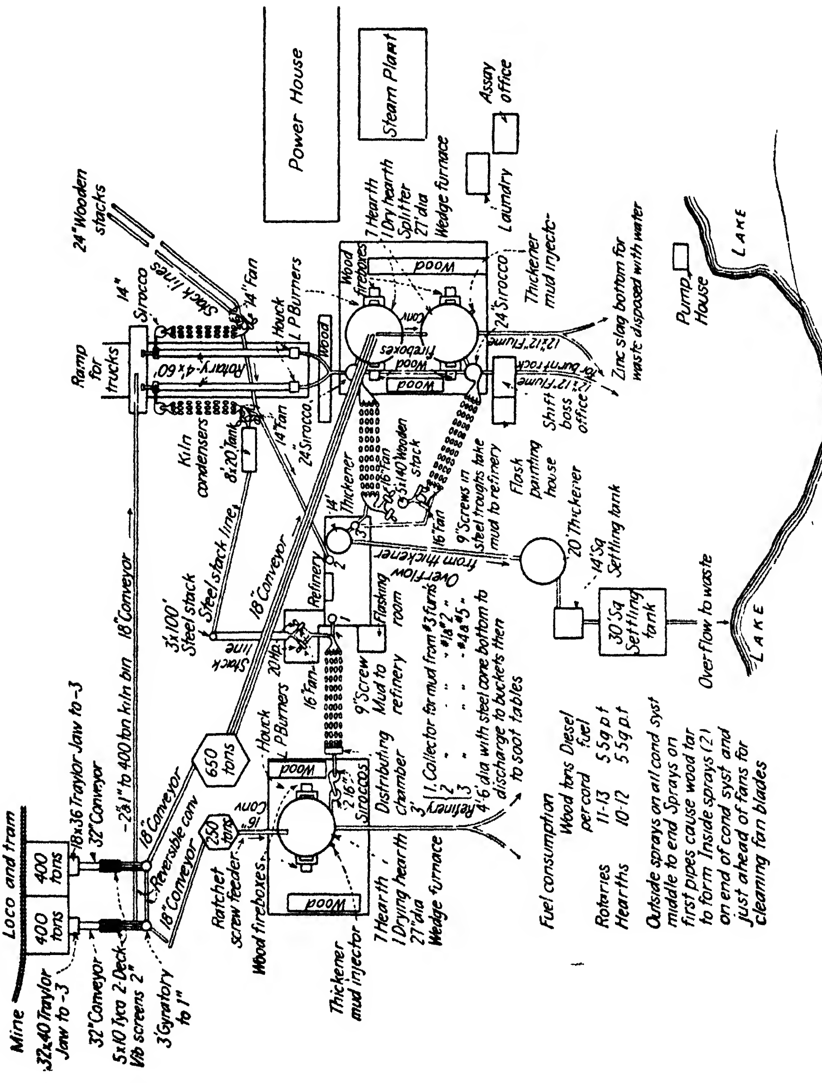

FIG. 10.—Pinchi Lake flow sheet. (Courtesy Consol. Min. & Sm. Co. of Canada.)

Pinchi Lake Mine, British Columbia, Canada.—Figure 10 shows in general th flow sheet of this installation. Furnace equipment consists of three 25 ft. diameter Wedge furnaces and two 46 in. × 60 ft. rotary furnaces. This plant, built within the past three to four years, is the largest quicksilver plant in the world, having a daily capacity of 1300 to 1400 tons.

The flow sheet is self-explanatory; however, several interesting features and innovations are noted. Because of difficulties of transportation, all furnaces were originally installed to be wood-fired. After some experimentation, fair results wer

obtained with a wood consumption of 11 to 15 tons of ore burned per cord of wood. Because of increasing difficulty in obtaining suitable wood, oil burners were later installed on all furnaces and the Wedges were fired one-half with oil and one-half with wood. The rotaries were converted to all oil-firing. Operation in general was improved by this change. Very short stack lines from the Wedge furnaces is at variance with most American plants, as satisfactory recoveries are obtained in the condensing units. In order to facilitate cleanup, screw conveyers have been installed under each condensing system to transport all mud and quicksilver to a central "refinery." Here it is hoed either manually or on a mechanical hoeing table. The hoed soot is pumped to the Wedges, where it is injected through a jet directly onto one of the hearths. Overflow water is settled in two thickeners, followed by a series of settling tanks. Each furnace has two exhaust fans arranged in parallel, one of which acts as a spare. These are located at the end of the condensing system. Because adequate water is available, all burned ore is sluiced away from the furnaces, the burned ore from the rotary furnace soaking pit being fed into the flume by shaker feeders similar to those used for feeding ore to the rotaries. The flumes are lined with preformed lead smeltery slag brick to minimize wear. Ore is delivered by electric haulage from the mine to two 400-ton coarse-ore storage bins. A 32 × 40 in. jaw crusher, with an 18 × 36 in. jaw crusher as a spare, reduces it to minus 3 in. and it is then conveyed to a 5 × 10 ft. double-deck vibrating screen with 2½- and 1-in. screens. The minus 2½-in. plus 1-in. product goes directly to two 100-ton fine-ore bins for the two rotary furnaces. All plus 2½ in. goes to a *T-Y* gyratory crusher or a Symons disk (which acts as a spare) delivering a minus 1-in. product. This is conveyed either to a 250-ton fine-ore bin ahead of one of the Wedges or to a 650 fine-ore bin to feed two of the Wedges. All power is generated on the property by several diesel generators totalling approximately 2000 hp.

Cordero Mine, Nevada.—The furnace used at this property is the three-zone Herreshoff furnace, described under Hearth Furnaces, and is the only furnace of this type used in quicksilver-ore reduction. It has a capacity of approximately 126 tons per day and owing to the utilization of waste heat shows excellent fuel consumption. The condensing system, shown in Fig. 11, is made up of 9-in. tubes, the hottest section made of 12-gauge black iron and followed by cast-iron and, finally, 24-gauge stainless steel (Type 317). The exhaust fan is located after the condensers and is followed by a 5 ft. diameter by 24 ft. high settling tank on top of which is mounted a 24-ft. stack. Owing to the flat topography, several re-elevations of the ore are necessary, for which conveyer belts have been used. The ore is delivered by truck to a small receiving bin from which it is elevated by conveyer to a 150-ton coarse-ore bin; at the bottom of this bin a shaking screen and feeder delivers the minus-1-in. material directly on to another conveyer belt and the plus-1-in. ore to a 9 × 21 in. jaw crusher, the product of which combines with the minus 1 in. on the same belt; this belt elevates the ore to a 250-ton steel fine-ore bin; a weightometer feeder under this bin feeds another conveyer which elevates the ore to the furnace. Because of the construction of this furnace, ore is discharged at approximately 300 to 350°F., and a conveyer is used to transport the burnt ore away from the furnace to a stock pile from which it is occasionally removed by truck or dragline. Power for all operations is generated on the property by Cummins diesel-generator units.

Sulphur Bank and Reed Mines, California.—These two mines, although having quite distinctly different types of ore, have one problem in common, and the same method has been adopted at each plant to overcome the trouble. The ore at the Sulphur Bank has a very high content of free sulphur. The ore at the Reed has an appreciable free sulphur content and, as well, as much as several pounds per ton of petroleum. The furnace at the Sulphur Bank is a 4 × 50 ft. rotary, and the one at

the Reed is a 4 × 60 ft. rotary. In the original installation at the Sulphur Bank and in an earlier installation at the Reed, the furnaces were arranged for counterflow operation. Experience showed, however, that the free sulphur and the petroleum burned in the upper or drying end of the kiln but burned incompletely, owing to lack of oxygen, thus causing the precipitation of sulphur and petroleum soot in the condensing system.

This situation was so troublesome that the kilns were rearranged for parallel flow in order that the ore, upon being fed to the kiln, is immediately exposed to the highest heat and most oxygen, thus more completely burning off the sulphur and petroleum. Although in this type of kiln, the lower end is used for soaking, advantage cannot be taken of the drying effect in the upper portion of a counterflow kiln, and fuel consump-

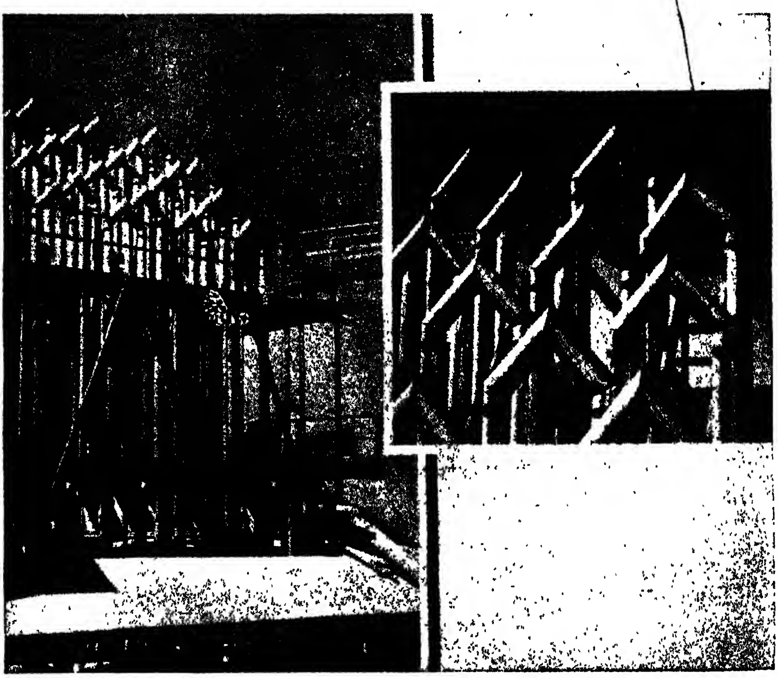

FIG. 11.—Cordero mine condensing system.

tion and temperature of gases leaving the kiln are both considerably higher. Fuel consumption in these operations ranges between 15 and 20 gal. per ton, and exit temperatures approximate 1000°F. This latter fact requires (or permits) that considerable cooling be accomplished before the gases reach the condensing system. "In the case of the Reed plant, longer than usual pipe runs between the kiln and cyclone type of collector and between the collector and a cast-iron condensing system act as the cooler so that gases enter the cast-iron system at near normal temperatures."

This is a special problem known only at these mines, and there have been no other successful parallel-flow rotary-kiln installations.

Red Devil Mine, Alaska.—The furnace at this mine is a 3 × 40 ft. rotary furnace of 20 to 25 tons daily capacity with 8-in. shaker feeder, 10-in. Sirocco dust collector. No. 25 American Blower Co. exhaust fan, cast-iron condensing system made up of 16 in. diameter pipes, two 10 ft. diameter by 20 ft. high redwood settling tanks, 110 ft

of 18-in. redwood stackline, and a 40 ft. high 18 in. diameter redwood stack. The furnace is fired with wood fuel, and consumption amounts to approximately 11 to 12 tons per cord of wood. Good combustion is obtained and, possibly because of the character of the wood used, no wood tars are condensed in the condensing system. Ore is hand-trammed and hoisted from the mine into a 20-ton coarse-ore bin which feeds an 8 × 15 in. jaw crusher. It is crushed to minus 2 in. and fed to a conveyer belt that elevates and feeds a 40-ton steel fine-ore bin directly over the furnace feeder. The capacity of this furnace is somewhat reduced by comparison with other installations of the same size for the following reasons: because of wood firing, the volume of the gases of combustion is considerably greater than for oil firing; the ore carries an average of 1 to 3 per cent arsenic and 5 to 10 per cent antimony, either of which may at times exceed twice these amounts, and thus requires a greater volume of air for oxidizing these volatile components; and the moisture content of the ore is relatively high (10 to 20 per cent). Because the cinnabar is intimately associated with the arsenic and the antimony, it is necessary to make a nearly complete elimination of these metals in order to effect a complete recovery of the quicksilver. Unless sufficient air is provided to oxidize the stibnite, it has a tendency to melt, thus causing the ore in the kiln to stick to the brickwork. Careful control of fire and draft, however, makes it possible to get a good elimination of all quicksilver from the ore without clinkering in the kiln. Because of the relatively large amounts of antimony and arsenic in the ore, and because it was found necessary nearly to eliminate it from the ore by roasting, a large bulk of the oxide of the two metals was collected in the condensing system. This bulky precipitate was a part of the soot and made recovery of the quicksilver from the soot considerably more difficult than is normally the case. By hand hoeing it was found that frequently less than 10 per cent of the quicksilver could be recovered so that two D retorts, which had been used in prospecting the mine, were put into use to burn the soot after hoeing. This provided a good recovery, however, and the procedure was adopted. Despite the large amounts of antimony and arsenic present, the contamination of the quicksilver by either of these elements was practically nil. Sampling of 1000 flasks showed no arsenic and 0.003 per cent antimony.

Hermes Mine, Idaho.—The reduction plant consists of two modern rotary furnaces, 4 × 64 ft., having a capacity of approximately 140 to 150 tons per day. With dry ore in the summer, this capacity is somewhat exceeded; however, during the spring thaw the ore is very wet and the tonnage may be 15 to 25 tons less than this. The kilns are oil fired with heavy oil (16 to 18° Bé.), and fuel consumption varies with the moisture content. The collectors are No. 11 Siroccos and are followed by American Blower Co. No. 30 exhaust fans. Condensing systems include forty 16 in. diameter by 12 ft. lengths of cast-iron pipe with 12 hoppers and 10 returns, set up as a double-row double-deck system. Two 10 ft. diameter by 20 ft. high redwood settling tanks with conical bottoms, in series, follow the cast-iron system. Redwood stack lines and stack follow the tanks. In order to lower the temperature and knock down any quicksilver in the settling tanks, several grids made up of 1 × 2 in. fir, with 2 in. square openings, were placed one over the other in the tanks. A spray of water introduced at the top of the tank made each tank a washing tower, and although little quicksilver is collected, it is reported to have justified the installation. Firing is effected through high-pressure oil burners, each kiln being equipped with a 15-hp. compressor for atomization. All dust collected in the collectors, amounting to about 500 lb. per day per kiln and being of too low value to warrant re-treatment, is sluiced away from the plant with water. The high-grade soot collected in buckets under the condensers is normally hoed on a water-heated hoeing table. The residue from this operation, plus other low-grade soot, is dried in a tunnel drier extending through the burnt-ore bin and returned to the fine-ore bin.

Concentration of Quicksilver Ores.—The general opinion, by most quicksilver operators and others who have investigated the possibilities, that concentration of quicksilver ores cannot compete with direct furnacing, has largely been borne out by the failure of this method to remain or to become firmly established. Like the development of furnacing and condensing equipment, most experimenting and most installations were made when the price of quicksilver was high and operators more prosperous. Consequently, it is reasonable to believe that better than average engineering was applied in the attempted development of concentration methods. Likewise, there was the counterpart of the "get by as cheaply as possible" retort builder whose concentration plant was not destined to efficient operation. There have been, therefore, several periods in which development advanced more rapidly than in others.

Although wet crushing and treatment of ores is known to have been carried on in Italian mines as early as the seventeenth century, little is known of the methods or results obtained. The first known American concentration plant was at the San Carlos mine (now a part of the New Idria mine) where riffle boxes and rockers were used in 1871. Other similar operations are reported from a number of localities until, in the period from 1910 to 1916, many mills were built.

Most of the mills built during this period were gravity-concentration plants. They employed many types of mills including Huntington, Chilean, ball, rod, or roll; some plants used no mills or depended upon screens or trommels to sort out coarse material. Classifiers were not always used, thus giving a mixed feed to the concentrator with resultant less efficient performance. Concentrators included several types of tables, Frue vanners, and occasionally jigs.

In a few plants, flotation cells were added in an attempt to recover values ordinarily lost in the slimes, and a few all-flotation plants were installed.

The results ot the mills operated during this period were similar in that they all showed poor recovery. In the straight gravity-concentration plants, the friability of cinnabar and the actual or attendant overgrinding of the ore caused large slime losses. The frequent failure to size the feed to the tables closely meant less efficient operation of the tables, and additional losses were incurred. The employment of flotation to recover slime losses was handicapped by the infancy of the flotation process at that time, the cost of fine grinding, and, in one case, by the exorbitancy of royalties demanded for the use of the flotation cell. Because of the variety of flow sheets used and differences in ore treated, it is difficult to estimate average recoveries made; however, they probably ranged from 25 to 85 per cent, with the better designed and larger mills approximating 60 to 70 per cent. Operating costs ranged from $0.50 to $1.25 per ton. When it is considered that roasting of the concentrates, either in retorts or by combining with furnace feed, and the cost and loss incurred in this operation is an addition to the milling costs, the comparison with direct furnacing is definitely in favor of the latter.

An excellent description of milling operations in this period is given by Bradley[11].

The advances made in flotation were in part responsible for increased interest in milling plants from 1927 to 1931. During this period, several flotation plants were built. The plant built at the Sulphur Bank mine in California was designed to overcome the problem of large amounts of free sulphur in the ore, an objectionable feature in furnacing. Despite several years of experimentation and operation, however, the mill was abandoned and direct furnacing reemployed.

During this same period and in the few years following, a number of gravity-concentration plants were built including the use of jigs of the Bendelari, Pan-American, and Southwestern types. The development of these jigs, with large capacity and efficient recovery and their successful use on gold dredges and in many metal mills

led to their application in several quicksilver-recovery plants. They were usually combined with trommels or shaking screens and riffle boxes, without any mills. Several of these plants were installed to treat old mine dumps or burnt-ore dumps. Recoveries obtained were of the same order as in previous concentration plants; however, their low initial and operating costs made them economically profitable operations.

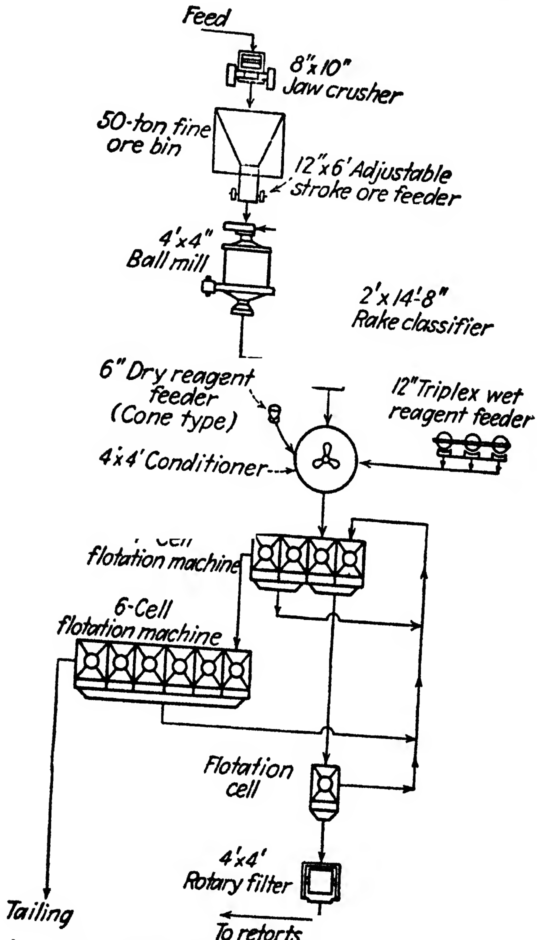

FIG. 12.—Beneficiadora de Mercurio, S.A., flow sheet.

In 1940, the Denver Equipment Co.[12] installed a modern flotation mill on the properties of Compañía Mercurio en Sain Alto and Beneficiadora de Mercurio, S.A., in Zacatecas, Mexico. The flow sheet of this mill is shown in Fig. 12. The ore occurs in sandstones and shales, cinnabar being the predominant sulphide with lesser amounts of metacinnabarite, pyrite, and arsenopyrite. Some graphitic and carbonaceous material also occurs in the ore.

A partial analysis of a sample of the ore showed: Hg, 0.55 per cent; As, 0.10; Fe, 4.30; insoluble, 74.60; S, 9.57.

The plant has a capacity of 60 tons per 24 hr. The ore is crushed to minus ½ in. and ground to minus 65 mesh at 67 per cent solids. The ball mill is in closed circuit

with the classifier, which overflows to the conditioner. Conditioning time is approximately three minutes, and all reagents are added to the conditioner in order to suppress the carbonaceous and gray slimes. Reagents used per ton are Yarmor F pine oil, 70 g.; potassium ethyl xanthate Z-3, 30; Reagent 105, 20; starch or Reagent No. 637, varies depending on free carbon content. Dilution of the circuit is held to 4:1, and a pH of 7.2 is maintained for best flotation results. Discharge from the filter carries approximately 15 per cent moisture and is retorted. Mill data over a representative period, Nov. 15 to Dec. 5, 1941, is shown in Table 7.

TABLE 7.—MILL DATA, BENEFICIADORA DE MERCURIO, SAIN ALTO, ZACATECAS, MEXICO

Product	Weight, %	Tons per 16 hr.	Hg, %	Recovery %
Heads	100.00	33.33	0.67	100.0
Concentrates	1.39	0.46	46.21	95.4
Tailing	98.61	32.87	0.03	4.6

The metallurgical results of this operation are interesting and show that modern flotation practice, possibly together with an especially amenable ore, can produce results approaching direct furnacing. If costs can be held sufficiently low to offset a sometimes greater loss, there is a definite place for flotation in the metallurgy of quicksilver ores.

Generally speaking, however, experience has shown that gravity concentration, at best, cannot approach direct furnacing, owing in part to slime losses and also to the inability of the concentrators to make a high recovery. Higher recovery can more easily be made at the sacrifice of grade of concentrate, a fact that has made economically profitable the operation of concentration plants in mines where furnaces are installed and operating. Very low-grade ores can be raised sufficiently to make them of furnace grade at relatively low cost and good recovery, as was done at the New Idria mine. Old mine dumps and burnt-ore dumps in 1938–1941 were mined by power shovel, trucked to a bin, passed over a grizzly set at 2 in. and a shaker screen with ⅝-in. openings. All coarse material was hand-sorted for high grade and the minus ⅝-in. then passed over a 42-in. Benedlari jig and thence to about 100 ft. of riffle boxes. The grade of product collected was 6 to 10 lb. per ton from 1 to 2 lb. per ton in the material as mined. Recovery was 40 to 60 per cent, but costs were low enough to justify the operation.

Flotation of quicksilver ores has been handicapped by the nonuniformity of most quicksilver ores and the cost of fine grinding. There is quite possibly a place for flotation if all factors are properly considered in advance. Unfortunately, large deposits of quicksilver ore, justifying a large milling plant with its low initial and operating unit costs, which are uniform, and moderately easy grinding, are not yet known.

Chemical Treatment of Ores.—The only wet chemical treatment process for the reduction of quicksilver which has received considerable attention depends on the solubility of metallic quicksilver or cinnabar in a solution of sodium sulphide and sodium hydroxide, although other alkaline sulphides may be used. The caustic hydroxide is necessary only in small amounts to secure the maximum solvent power of the sodium sulphide over the cinnabar. The reaction is represented by the equation

$$HgS + Na_2S = HgS.Na_2S$$

and the recovery of the quicksilver from the solution is made by precipitation with aluminum according to the equation

$$3HgS.Na_2S + 8NaOH + 2Al = 3Hg + 6Na_2S + 2NaAlO_2 + 4H_2O$$

Although the electrolytic deposition of the quicksilver from the alkaline sulphide solution has been considered, the precipitation by aluminum seems to have an advantage due to the regeneration of the Na_2S.

Thornhill[13] has described the recovery of quicksilver from amalgamation tailings using this process in an operation at the Buffalo mines, Cobalt, Ontario, during 1915. This is the only commercial-scale operation of this type known, and although results were reported as satisfactory, it was not applied to cinnabar ore.

Various experiments have shown as many results; however, it is not generally believed that, because of chemical-consuming constitutents of many ores, the cost of fine grinding, irregularity as to composition of ore feed (so common in many quicksilver mines), difficulties in filtering, cost of aluminum, and over-all recovery, the process can compete with modern furnace treatment of quicksilver ores.

Mercurial Poisoning.—Inasmuch as all persons exposed to quicksilver are subject, in greater or lesser degree, to mercurial poisoning, or salivation, as it is usually called around the mines and reduction plants, certain precautions and fundamentals of design or operation should be considered.

The principal symptoms of chronic mercurial poisoning, usually developing in this order until all three are evident, are stomatitis, psychic irritability, and tremors. Davenport and Harrington[14] report in considerable detail each of these symptoms and further point out the variation in sensitivity of different people to mercurial poisoning. Continued exposure to an atmosphere contaminated with quicksilver vapor is recognized as being more harmful than intermittent exposure inasmuch as elimination of quicksilver entering the body through the respiratory passages, the gastrointestinal tract, or through the skin is slower than absorption.

Figures on what is considered to be a dangerous contamination, likewise, vary over a great range depending on the sensitivity of the individual and whether or not he has previously been exposed. The figures range from 0.1 mg. per cu. m. of air up to 10 or 20 mg. per cu. m.; however, the California Industrial Hygiene Service and the Industrial Accident Commission of California have adopted a limit of 0.15 mg. per cu. m. of air[15].

Precautions to be taken to prevent mercurial poisoning are listed[14] and generally include personal cleanliness and good housekeeping around the reduction plant. In design and operation of the various types of plants, leakage of fumes or dust should be prevented, good ventilation provided in all dangerous areas, protective clothing and respirators worn by workmen when subject to exposure, and mechanical soot-treating devices used to the greatest extent in order to reduce exposure.

The fact that attention has been devoted to this subject with successful results is evidenced in the compensation insurance rates for workmen in this classification in California, where three mines pay between \$2.98 and \$3.86 per \$100 of pay roll, depending on the experience rating of the mine. This compares with surface-mining rates of \$3.50 to \$4.50 and underground-mining rates of \$7 to \$9 per \$100 of pay roll.

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CHAPTER XVII

CHLORINE METALLURGICAL PROCESSES

By Donald M. Liddell[1]

Chlorine as a metallurgical reagent appears to have lost ground during recent years, and much of what follows is of historical rather than operating interest. However, it is a question in the author's mind whether the great decrease in price of chlorine and the large sources of supply that will be available after the war do not warrant reinvestigation of the applicability of chlorine processes to present-day metallurgy.

EARLY HISTORY

Chlorine has been used almost exclusively for the recovery of gold and silver. It has been used to some extent in the treatment of low-grade copper ores, but never in a major metallurgical process for the recovery of copper. The use of chlorine in the metallurgy of other base metals has been subsidiary.

High-grade gold and silver ores and high-grade base-metal ores containing small or large amounts of gold and silver are usually smelted to recover the metals. Chlorine has been associated only with hydrometallurgical processes (including amalgamation), usually for low-grade ores, but sometimes for high-grade siliceous ores remote from other facilities for treatment.

The earliest hydrometallurgical process for treating gold and silver ores was amalgamation. The date when mercury was first used for this purpose is unknown. Amalgamation of gold was known to the Romans and was recorded by Pliny, but no reference is made to silver. For the oxidized ores near the surface—where the gold and silver were in metallic condition or the silver occurred as a haloid—this process was simple, but when deeper mining reached sulphide ores another method had to be devised to put these metals into a condition to be amalgamated.

The first recorded use of mercury in the metallurgy of silver, and in connection with it the first recorded use of chlorine in any metallurgical process, occurs in a treatise entitled "De la Pirotechnia," by Vanoccio Biringuccio, published in Venice in 1540.[2] In this treatise it is stated that the ore (previously roasted, if refractory) was finely ground in a stone mortar, screened wet, and dried. The dry ore was moistened with vinegar or water, in which had been dissolved mercuric chloride, copper sulphate, common salt, and sometimes ferrous sulphate. The ore pulp was then covered with mercury and ground, or stirred, in the mortar for an hour or two. The tailings were washed away with water, and the silver was recovered by retorting the amalgam.

The Patio process for the treatment of silver ores, involving the same chemical reactions as those in the process just described, was invented by Bartolomé Medina, a miner of Pachuca, Mexico, in 1557.[3] The invention of this process is credited to

[1] This chapter is a major revision of the chapter contributed by the late Stuart Croasdale to the first edition of the handbook.

[2] Percy, "Metallurgy of Silver and Gold," pp. 559–562, London, 1880.

[3] *Op. cit.*, p. 561.

Medina, in a report by Luis Berrio de Montalvo, addressed to the Viceroy of Mexico and printed in Mexico in 1643, and also in a memoir by Díaz de la Calle to Philip IV, printed in Madrid in 1646. Montalvo intimates that Medina derived his information from Spain that silver could be obtained from its ores by means of mercury and salt. The process was especially adapted to the arid regions of Mexico and South America, where fuel and water were scarce and transport expensive. It is still used to some extent in these countries and will be described in detail later.

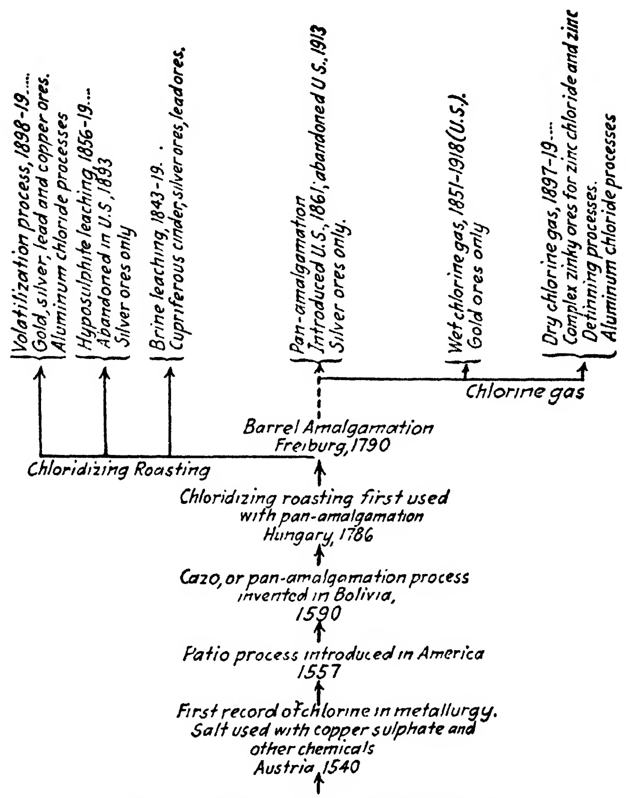

FIG. 1.—The chlorine metallurgical tree.

The "Cazo" or caldron process was invented in 1590[1] by a priest, Alvaro Alonzo Barba, at Tarabuco, 24 miles from La Plata, Peru (now Bolivia). This process was the ancestor of the pan-amalgamation process. It was particularly adapted to the rich surface ores of that district containing chloride of silver, and it was also applied to silver sulphide ores to some extent. The process was conducted in a vessel made wholly of copper, or having a copper bottom. This vessel or caldron was provided with a vertical shaft, to which radial arms were attached for agitating the ore. Finely ground ore, water, and common salt were mixed together to the consistency of a thin pulp and placed in the caldron.

[1] BARBA, ALVARO ALONZO, "El Arte de los Metales," 3d book, Spain, 1640; DOUGLAS and MATHEWSON, English translation, pp. 149–194, New York and London, 1923.

The caldrons, usually four in number, were placed on top of an adobe furnace built like a cook stove, and heated so as to keep the ore pulp at the boiling point. Mercury was added, and the boiling pulp was stirred continuously for several hours, after which time the amalgamation was completed. The caldron was removed from the furnace, the tailings washed away with water, the amalgam recovered, and the process repeated with a new charge of ore. The active chemical reagents were the copper of the caldron and the boiling solution of common salt. The silver chloride in the ore was dissolved in the hot brine and reduced to the metallic state by the copper of the caldron, and then amalgamated by the mercury. The cuprous chloride formed was also dissolved by the salt solution and became active in converting the silver sulphide minerals into the chloride, although if a large amount of sulphide minerals were present preliminary roasting was recommended on account of the consequent loss of mercury. In later years, iron was added to the caldrons to reduce and recover mercury that had become soluble or floured.

The Krohnke process, in which cuprous chloride was added to the hot salt solution to decompose the sulphide minerals, was introduced in Chile in 1860. The silver was recovered by means of zinc or lead used in the form of amalgam.

Chloridizing Roasting.—In Europe, where fuel, mechanical appliances, and better operating facilities were available, more complicated processes were developed to treat ores. Chloridizing roasting of silver ores was first introduced in Vienna by Born, and combined with the Cazo process in 1786 at Chemnitz in Hungary. The Cazo process was soon superseded in Europe by the barrel-amalgamation process, which was first installed on a large scale in 1790 at Halsbrucker Hütte, near Freiberg, Saxony. Metallurgical works had been established at this point since 1710, and chloridizing roasting with barrel amalgamation was used not only for the ores but also for metallurgical products, such as matte, blister copper, and speiss.

The chloridized ore or furnace product, still containing an excess of salt, was rotated in a wooden barrel with water and scrap iron until the silver was reduced to a metallic state. Mercury was then added to recover the silver as amalgam. Owing to the base metals present, which were also chloridized in roasting and reduced by the scrap iron, the bullion obtained was very low grade. Attempts to "destroy" the base metals by roasting at a higher temperature resulted in considerable loss of silver through volatilization with the base-metal chlorides, and the chloridizing roast was eventually used only on the low-grade ores containing the least amount of volatile base metals.

This led to the invention of the *Augustin process* and its introduction at the Gottesbelehnung Hütte near Mansfeld, Germany, in 1843. Later in the same year, the process was introduced at the Freiberg works. In this process ores were roasted with salt and then leached with a saturated solution of common salt. The silver chloride passed into solution, from which the silver was precipitated by metallic copper. The process was introduced at both Mansfeld and Freiberg to recover the silver from the copper mattes, but, owing to the imperfect extraction of the silver by the brine, it was soon abandoned and was superseded by the *Ziervogel process* in 1848, which was applied more particularly to mattes and furnace products than to the ores themselves. In this process no salt was used. The iron and copper were converted into oxides and the silver into sulphate by careful oxidizing roasting. The silver was then leached out by warm water and precipitated on copper.

Hyposulphite Leaching—Patera Process.—In 1848, Dr. John Percy, of London, suggested the use of sodium or calcium thiosulphate—incorrectly called hyposulphite—as a solvent for the chloride of silver after ores had been subjected to a chloridizing roast. The first practical application of this suggestion was made in 1856 by von Patera on the rich silver ores of the Joachimsthal district, Bohemia. To reduce

losses by volatilization, von Patera introduced steam into the furnace during the chloridizing roasting. This process was first introduced in America by Ottokar Hofmann, in 1868, at La Dura, Sonora, Mexico; it was gradually adopted at other mines in Mexico and the United States, reaching the zenith of its application during the succeeding 25 years, until the demonetization of silver by the government of the United States in 1893 closed every leaching plant in this country that had been treating silver ores.

Up to this time, and for a number of years afterward, gold in ores that had been subjected to a chloridizing roast was supposed to be converted into the chloride, which decomposed into chlorine and metallic gold at a temperature below 300°C. Hence, if gold occurred in silver ores, it was converted into metallic gold by chloridizing roasting and was not recovered by any of the solvents used for the extraction of silver.

Plattner Process.—Plattner proposed converting the gold into chloride by means of chlorine gas and extracting it with water. This process was introduced in Silesia, Germany, in 1851. The ore was either roasted "dead" or, if it contained silver, it was chloridized by roasting with salt. The silver was first leached out by brine or "hyposulphite" solution, then chlorine gas was applied to the ore in the vats. The gold was recovered by subsequent leaching with water and precipitating by means of ferrous sulphate (see Wet Chlorine-gas Processes).

Longmaid-Henderson Process for Copper Ores.—The treatment of copper ores by chloridizing roasting was first patented by Longmaid in 1844 and was first applied to the extraction of copper from pyritic residues or calcines by William Henderson of Scotland in 1859–1860.[1]

Pyrites from Spain and Norway, which were used throughout Europe for making sulphuric acid, contained 3 to 8 per cent of copper. After the pyrites were roasted for the manufacture of sulphuric acid, the residues were again roasted with salt by the Henderson process, to convert the copper into chloride. The chloridized ore was then leached with water or dilute acid, and the copper was precipitated from the solution by iron.

The gases from chloridizing roasting contained sulphurous acid, hydrochloric acid, and chlorine. To prevent these gases from becoming noxious to the neighborhood, and to utilize their acids, they were passed through coke towers sprayed with water, which collected not only the acids but any volatilized metallic chlorides as well. The water from the scrubbing towers was used for leaching the chloridized ore.

This process was patented in the United States in 1866 and was in constant use, both in this country and Europe, for over 60 years. It will be further described under the paragraph on copper ores in the section on Chloridizing Roasting and Leaching Processes.

When the residues or ores contained silver, that metal was precipitated from solution as an iodide by the *Claudet process* before the precipitation of the copper.

Hunt & Douglas Process.—About the same time, 1862, ferrous chloride was suggested by Schaffner and Unger, of Germany, as a solvent for copper in ores. This method was developed later in the United States into the Hunt & Douglas process. It was designed to treat oxidized copper ores with siliceous gangue.

Ferrous chloride was made by dissolving copperas (ferrous sulphate) and common salt in water. An excess of salt was then added, and the sulphate of soda was removed as much as possible by crystallizaton. This solution, therefore, became a brine solvent containing a soluble base-metal (ferrous) chloride. The process was appli-

[1] EISSLER, MANUEL, "The Hydrometallurgy of Copper, being an account of processes adopted in the hydrometallurgical treatment of cupriferous ores, including the manufacture of copper vitriol, with chapters on the sources of supply of copper and the roasting of copper ores," pp. 87–104, London and New York, 1902

cable to raw ore containing oxide or carbonate of copper and was later applied to the separation of silver and copper in roasted matte, because silver minerals are likewise soluble in the brine as prepared. The copper was precipitated on scrap iron in the usual manner. If silver was present, it was first removed by precipitation on copper.

The Hunt & Douglas process passed through many modifications on account of the difficulty of treating ores containing any carbonate of lime or magnesia, both of which precipitate the iron from the solvent. It was abandoned many years ago and was replaced by smelting and electrolytic refining. Acid leaching has replaced it in hydrometallurgy.

The Doetsch process,[1] using ferric chloride as a solvent for copper, was invented about this same period to treat the sulphide ores at Rio Tinto. An attempt was made in 1914 to revive this process under the name of the *Slater process*,[2] but it did not pass the experimental stage. The feature of the Slater process was the regeneras tion of the ferric chloride. A lixiviant containing ferric chloride and hypochlorou- acid was produced by suspending ferric hydroxide in the anode compartment of a cell in which a salt solution was electrolyzed. After the dissolution of the copper from the ore, ferric hydroxide was precipitated from the lixivium by means of the sodium hydroxide produced in the cathode compartment of the electrolytic cell. Under the highly oxidizing conditions in the solution, ferric hydroxide can be preferentially precipitated in this manner without precipitating any of the copper. The ferric hydroxide precipitate was returned to the circuit in the anode compartment for the generation of new lixiviant, and the copper was recovered from solution by the usual methods. The only reagent required was common salt. The process was not adapted to basic ores. A slight modification of this process was developed by the Midland Ores & Patents Co.[3] at Waverly, N. J., in which the solution containing ferrous chloride, after precipitating the copper on iron, was regenerated direct by electrolysis, yielding ferric chloride for new lixiviant and metallic iron for copper precipitation (see page 540).

The Hoepfner process for copper ores[4] was introduced in Germany in 1891. The copper ore was leached in revolving barrels with a solution of cupric chloride and salt or calcium chloride. The lixivium was purified by precipitating the silver on metallic copper, by cooling to separate the lead chloride, by adding powdered limestone to precipitate the arsenic, antimony, and bismuth, and by the use of air in a special manner to precipitate the iron as oxide. It was then electrolyzed to precipitate part of the copper as pure metal, and to regenerate cupric chloride for leaching new ore. Owing to difficulties in manipulation, the process was not a commercial success.

Hoepfner Process for Zinc Ores.[5]—The ore was roasted with salt at a temperature not to exceed 650°C. and leached with hot water. The solution was purified by cooling to 5°C. to crystallize out the sodium sulphate, by adding bleaching powder and marble dust to precipitate the iron and manganese, and by adding powdered zinc to precipitate the other electronegative metals. The purified zinc and sodium chloride solution was electrolyzed for the production of metallic zinc and the recovery

[1] Cumenge, Notes sur le Rio Tinto, *Ann. mines*, Vol. 96.

[2] Morse, H. W., The Slater Leaching Process for Copper Ores, *Mining Sci. Press*, Jan. 24, 1914, p. 181.

[3] Leaching at Yerrington, *Mining Sci. Press*, July 17, 1915, p. 94; Perry, R. W., Leaching Oxidized Copper Ores with Ferric Chloride, *Mining Sci. Press*, May 17, 1919, pp. 669–674; Middleton, Percy R., Ferric Salts as Solvents in the Leaching of Roasted Copper Ores, *Eng. Mining Jour. Press*, Sept. 9, 1922, pp. 452–453.

[4] *Z. angew. Chem.*, 1891, p. 160; *Offizielle Zeitung der internationalen elektrotechnischen Austellung*, Frankfurt am Main, No. 27; Eilers, Karl, Hoepfner's Electrolytic Copper Process, *Eng. Mining Jour.*, Apr. 30, 1892, p. 471.

[5] Guenther, E., Electrolytic Zinc Extraction by the Hoepfner Process, *Eng. Mining Jour.*, May 16, 1903, pp. 750–752; *Mineral Ind.*, Vol. 6, pp. 668 and 675; Vol. 7, p. 743; and Vol. 9, p. 688.

of chlorine to make bleaching powder. The process was used for a short time in Europe.

Swinburne-Ashcroft Process for Complex Ores.—The use of chlorine gas in the metallurgy of lead, zinc, and other base metals was brought into commercial prominence by Swinburne and Ashcroft of England, who obtained their first patents in 1897.[1] In the original process, as operated at Broken Hill, Australia, dry chlorine gas was applied under pressure to the dry and coarsely pulverized sulphide ore in a closed shaft furnace known as the "transformer." The chemical reactions involved are strongly exothermic and supplied all the heat necessary for operation. By regulating the flow of chlorine gas to the supply of fresh sulphide ore, a temperature of 600 to 700°C. could easily be maintained in the transformer.

The reaction between dry chlorine gas and a mineral sulphide results in the formation of a metallic chloride and free sulphur, as shown by the equation

$$XS + Cl_2 = XCl_2 + S$$

At the temperature named, the sulphur distilled from the top of the transformer and the fused metallic chlorides, with the gangue in suspension, were tapped from the bottom. The metals were recovered by substitution; the fused chlorides, as they came from the transformer, were stirred into a bath of molten lead, which decomposed the precious metal chlorides and recovered these metals in the form of a high-grade lead bullion; from the lead bath the fused chlorides were drawn to another kettle and treated with zinc to recover the lead; the remaining chlorides were then dissolved in water and treated with chlorine gas to oxidize the iron and manganese; zinc oxide, obtained by roasting high-grade blende, was added to this solution to precipitate the iron and manganese as oxides, which were removed, along with the gangue of the ore, by filtration. As will be seen by following this line of substitution, all the original chlorine was ultimately combined with zinc, and the filtrate from the iron and manganese oxides was a commercially pure solution of zinc chloride. In the final phase of this process, the zinc-chloride solution was evaporated to dryness and the zinc chloride fused and electrolyzed for the recovery of metallic zinc and the regeneration of the chlorine gas.

The process was cyclic. There was no appreciable loss of chlorine at any stage of the operations, and all the substitution metals were produced by the process itself, but the process did not prove successful as designed and operated. Its operation was limited to sulphide ores or concentrates carrying not over 30 per cent gangue, in order to maintain the temperature required.

A modification of this process was developed by *Baker and Burwell*, of Cleveland, Ohio, in 1904–1908.[2] The finely pulverized dry ore was placed in a porcelain-lined tube mill provided with lead-lined trunnions, and supplied with flint pebbles. Low-grade complex ores were treated, and in the absence of a high percentage of sulphur the temperature was kept down to 100°C. Dry chlorine gas was admitted to the tube mill, and chemical action began at once. As the tube mill revolved, the pebbles ground off the metallic chlorides as fast as formed and constantly exposed fresh

[1] SWINBURNE, JAMES, Chlorine Smelting, with Electrolysis, *Trans. Faraday Soc.*, July 1, 1903; *Mining Sci. Press*, Aug. 8 and 15, 1903; *Electrochem. Ind.* (now *Chem. Met. Eng.*), Vol. 1, pp. 412–413, August, 1903; Vol. 2, p. 404, October, 1904; Vol. 3, pp. 63–66, February, 1905; *Eng. Mining Jour.*, Aug. 1, 1903; STEINHART, O. J., "Chlorine Smelting," *Mining Sci. Press*, Nov. 28, 1903; ASHCROFT, E. A., *Trans. Inst. Mining Met. (London)*, June 19, 1901; *Mineral Ind.*, Vol. 9, pp. 692–693; Vol. 10, pp. 267 and 677–682.

[2] BAKER, CHARLES E., A New Application of Chlorine in Metallurgy, *Trans. Am. Electrochem. Soc.* Vol. 12, pp. 115–163, October, 1907; *Electrochem. Met. Ind.* (now *Chem. Met. Eng.*), Vol. 5, p. 448, 1907; Vol. 6, p. 433, 1908; BAKER and BURWELL, Electrolytic Chlorination Process, *Mining Sci. Press*, Feb. 6 and 20, 1905.

surfaces of ore to the action of the chlorine; they also broke up any lumps that might be formed. The free sulphur that was formed remained with the ore. If the temperature was allowed to get too high, considerable sulphur chloride was formed, which distilled off at about 150°C.

After chlorination was completed, the ore was discharged from the tube mill and leached with water, thus giving a clean solution of metallic chlorides free from sulphur and gangue. The metals were recovered from the aqueous solution by substitution. The gold and silver were precipitated on copper, the copper on lead, and the lead on zinc. After oxidation with chlorine gas, the iron and the manganese were precipitated by means of zinc oxide, and the zinc and the chlorine were recovered by the electrolysis of the fused chloride as in the Swinburne-Ashcroft process. A couple of experimental plants were erected in Montana in the years that followed, but, owing to operating difficulties, they did not prove successful. The most serious difficulties were to evaporate zinc chloride solution without the formation of basic salts and the consequent loss of chlorine as hydrochloric acid, and also the development of a satisfactory cell for the electrolysis of the fused zinc chloride.

About this time, John L. Malm, of Denver, Colo., began experimenting with the Baker-Burwell process, which he greatly modified and developed. This will be described as the *Malm process*[1] in the section on Dry Chlorine-gas Processes.

Pohlé-Croasdale Volatilization Process.—Loss of metals from volatilization during chloridizing roasting was known already when Plattner undertook a study of the conditions and extent of this loss in an elaborate series of experiments on both oxidizing and chloridizing roasting. The results of his experiments were published in his "Metallurgische Rostprozesse" (1856). He mentioned considerable loss of silver chloride when it came in contact with other easily volatilized chlorides and discussed at length the volatile products of the chloridizing roasting, but he failed to record any loss of gold by volatilization.

Loss of gold by volatilization was recognized from time to time[2] and was the source of serious monetary loss in treating gold-silver ores by chloridizing roasting, but the cause of this loss seemed to be little understood. It was generally attributed to tellurium,[3] and not to chlorine, because the chlorides of gold were supposed to decompose into the constituent elements at a temperature below 300°C.; therefore, all gold should remain in the ore in metallic condition. The first person to recognize chlorine as the source of this trouble was C. H. Aaron,[4] but after many experiments on roasting California gold ores with salt he came to the conclusion "that gold is volatilized in some form not easily condensable."

Christy[5] investigated this subject in the best chlorination mills in California as well as in the laboratory during the early eighties, and came to the conclusion that losses of both gold and silver increase (1) with increased percentage of salt added during the roast; (2) with increase of time and temperature during roasting; and (3) when salt is added after a long oxidizing roast instead of at the start. Christy qualifies the last statement by saying that, "while there is a rapid volatilization of gold and silver when

[1] Traphagen, F. W., Dry Chlorination of Sulphide Ores, *Mining Sci. Press*, April 10, 1909, p. 522; Herrick, R. L., The Malm Dry Chlorination Process, *Mines and Minerals*, January, 1910, p. 370; Ionides, S. A., Dry Chlorination of Complex Ores, *Mining Sci. Press*, May 27, 1916, pp. 781–787; Maier, C. G., Possibilities of Dry Chlorination of Oxidized Zinc Materials, *Eng. Mining Jour.-Press*, Vol. 115, pp. 51–54, January, 1923.

[2] Christy, S. B., The Losses in Roasting Gold Ores and the Volatility of Gold, *Trans. A.I.M.E.*, Vol. 17, p. 8, 1888–1889; Debray, H., Note sur le chlorure d'or, *Compt. rend.*, Vol. 69, p. 984, 1869.

[3] Küstel, Guido, Roasting of Gold and Silver Ores and the Extraction of Their Respective Metals without Quicksilver, p. 57, San Francisco, 1880; Christy, *op. cit.*, p. 3.

[4] Aaron, C. H., "Leaching Gold and Silver Ores, the Plattner and Kiss Process, a Practical Treatise," p. 121, San Francisco, 1881.

[5] Christy, *op. cit.*, pp. 3–44.

salt is added at the end of the roast, the gold chloride is quickly decomposed by the SO_2 gases and by the raw ore itself in the cooler end of the furnace, and the gold is redeposited in metallic form, so that the actual loss is not so great as when salt is added at the beginning of the roast."

Stetefeldt[1] expressed his opinion that the gold escaped as a double salt, and, if this were true, the loss of gold depended on the volatility of the chloride with which the gold chloride was combined.

In an earlier treatise,[2] Aaron states that the base metals are chloridized by chloridizing roasting, but they are not volatilized to any extent, while Küstel[3] takes the opposite view and states that "base metals as sulphates take up their share of salt and consume a large portion, but, as their chlorides are volatile, the salt is a means of getting rid of a great deal of the metals during roasting which are not desirable in the ore for subsequent treatment of silver."

The foregoing constitutes a brief summation of the knowledge of volatilization up to 1898. Much that is recorded is contradictory. There was no thought of making a commercial extraction by volatilization, and the recovery of the volatilized chlorides, if attempted, was only a phase of the general treatment of the ores.

In 1891–1893 Croasdale discovered that a commercially complete (above 90 per cent) volatilization of gold could be obtained from Cripple Creek ores by roasting with salt. About the same time, Pohlé independently obtained similar results with silver ores from Aspen, Colo. Systematic investigation of the volatilization of metals as chlorides was begun by these men in 1898 and was carried on with a large-scale experimental plant until 1903.[4] Numerous investigators[5] have worked on this process since that time. The process will be further discussed in the section on Chloride Volatilization Processes.

CHLORIDIZING PROCESSES FOR RAW ORES

With the exception of the Malm process, chlorine processes for raw ores of the precious metals are necessarily confined to the treatment of surface ores, or to clean gold and silver sulphide ores in which the gold and silver sulphide minerals are not combined with base-metal sulphide minerals. To obtain a commercial recovery of

[1] STETEFELDT, C. A., The Amalgamation of Gold Ores, and the Loss of Gold in Chloridizing Roasting, with Especial Reference to Roasting in a Stetefeldt Furnace, *Trans. A.I.M.E.*, Vol. 14, pp. 336–351, 1886.

[2] AARON, C. H., "A Practical Treatise on Testing and Working Silver Ores," San Francisco, 1876, pp. 35–36.

[3] KÜSTEL, *op. cit.*, p. 29.

[4] CROASDALE, STUART, Volatilization of Metals on Chlorides, *Eng. Mining Jour.*, Aug. 29, 1903, pp. 312–314; Sept. 19, 1903, p. 420; *Mining Mag., London*, March 1914, pp. 200–204; MATHER, HENRY A., *Eng. Mining Jour.*, Sept. 5, 1903, and Oct. 17, 1903, p. 576; HAWKINS, EDWIN N., *Eng. Mining Jour.*, Oct. 3, 1903, p. 490; ROSE, SIR T. K., "Metallurgy of Gold," p. 291, London, 1915.

[5] VARLEY, THOMAS, and others, *U. S. Bur. Mines Bull.* 211, 1923; the chloride volatilization process of ore treatment, being a complete compilation of the work that has been done on this process; LAYING, HARAI R., Chloridizing Processes, *Mining Sci. Press*, Jan. 17, 1920, pp. 77–83; Chloride Volatilization Process, *Mining Sci. Press*, Aug. 27, 1921, p. 284; Thermal Requirements of Chloridizing Volatilization, *Mining Sci. Press*, Feb. 25, 1922, pp. 264–266; Chloridizing Volatilization—Some Experiments and Their Practical Application, *Eng. Mining Jour.*, Nov. 12, 1921, pp. 764–770; BRADFORD, ROBERT H., The Volatilization Process at the Pope-Shenon Mine, *Mining Sci. Press*, Aug. 20, 1921, pp. 263–266; VARLEY, THOMAS, and C. C. STEVENSON, Development of the Chloride Volatilization Process by the U. S. Bureau of Mines, *Eng. Mining Jour.*, June 11, 1921, pp. 991–993; VARLEY, THOMAS, Chloride Volatilization, *Eng. Mining Jour.*, Feb. 18, 1922, pp. 276–278; GAHL, RUDOLF, Heat Requirements in Chloridizing Volatilization, *Eng. Mining Jour.-Press*, June 3, 1922, pp. 957–958; RALSTON, OLIVER C., Heat Requirements of Chloridizing Volatilization, *Eng. Mining Jour.-Press*, Apr. 15, 1922, pp. 614–616; HOWE, BEN, Gold Recovery by Volatilization, *Monthly Jour., West Australian Chamber of Mines*, December, 1912; *Mining Mag., London*, March, 1913; *Mining Sci. Press*, Mar. 29, 1913, p. 484; Oct. 1913, p. 535.

the gold and silver, the base metal sulphide minerals should not exceed 2 or 3 per cent; if more than this amount, concentration or roasting should precede the chloridizing process. Ores in which the silver is combined with arsenic and antimony as sulphides must be treated by chloridizing roasting to liberate the silver, or leached with alkaline sulphides. Base ores containing carbonates of lime and magnesia are not adapted to these processes, owing to their precipitating action on the metallic chlorides, which prevents reaction on the silver minerals. The gradual disuse of these processes has been brought about by the world-wide depletion of surface or suitable ores and the necessity of other methods of treatment for the complex sulphide ores that come with deeper mining; also by the possibility of treating lower grade ores on a larger scale at less cost by the cyanide process. Base-metal recoveries are made with the Malm process.

The Patio process is still used in isolated districts of Mexico and South America, but with modern machinery and methods of transportation it has been almost completely replaced by the cyanide process and by the custom-smelting plant. A complete description of this process is given on page 517. Therefore, a brief outline of its relationship to chlorine metallurgy will suffice here.

The salt and copper sulphate react to form sodium sulphate and cupric chloride. Some cuprous chloride is formed by the action of mercury on cupric chloride, and this is dissolved by the brine in the ore pulp. Both cupric and cuprous chlorides react on the sulphides of silver, forming silver chloride and copper sulphide. The silver chloride is dissolved by the brine in the torta, and the silver is precipitated in metallic form by the mercury, after which it is immediately amalgamated. Mercuric and mercurous chlorides are formed by the chemical reactions. Considerable silver sulphide is said to be reduced directly to metallic silver by the mercury, with the formation of mercuric sulphide.

The recovery of silver by this process will range from 75 to 80 per cent on favorable ores, but will drop below 60 per cent on ores containing an appreciable amount of base-metal suphides, particularly blende or arsenical and antimonial sulphide minerals.

There is a chemical loss of mercury in the form of soluble chlorides, as well as a mechanical loss due to the flouring of the mercury by surface chemical action of sulphide minerals, but the total loss is not so much as would be expected. It is said to amount to about one and one-half times the silver recovered.

This process is applicable only where labor and the few necessary supplies are cheap, equipment and freight are costly, and time of little importance. For example, the Noche Buena and Feliz Ano mines in the Totolapam district, about 75 miles east of Oaxaca City, Mex., in 1925 had in active operation six patios and were preparing to build six more. Extraction by the patio process was reported by the manager to be unusually high. Excessive freight rates, by muleback transportation, on stamp-mill concentrates caused the mine owners to enlarge their patio facilities.[1] The writer has not been able to obtain recent information.

The pan-amalgamation process was evolved from the "cazo" or caldron process. In Europe, where it was first used, the amalgamating was done in revolving barrels and was known as the "barrel-amalgamation" process. Pan amalgamation seems to have been an American development, and it was first operated in the United States at Washoe, Nev., in 1861. For a long time it was known as the "Washoe process."

The "pan" was made wholly of cast iron, or with a cast-iron bottom and wooden sides. In either case the bottom was made hollow for the introduction of steam to heat the charge. Cast-iron mullers for grinding, stirring, and amalgamating the

[1] *Eng. Min. Jour.-Press* (Sept. 5, 1925), 386.

ore were attached to a vertical shaft in the center of each pan. The capacity of each pan ranged from 0.5 to 2 tons of ore and was usually about 1½ tons.

The ore was first crushed by jaw crushers and then by stamps or ball mills. If crushed wet, the excess of water was removed by settling tanks. The crushed ore from the settling tanks was then shoveled into the pans. Salt and copper sulphate were added in the ratio of 5 to 10 lb. of salt and 2½ to 5 lb. of copper sulphate per ton of ore. When the ore is free from interfering minerals, the salt has been reduced as low as 2 lb. and the copper sulphate to 1¼ lb. per ton. Water was added in sufficient quantity to make a thin mud, and steam was admitted, not only in the jacketed bottom of the pan, but sometimes into the ore itself, until the charge in the pan was maintained at the boiling point. The grinding and stirring of the charge was continued for 2 or 3 hr., in which time the chemical action was completed.

Mercury, equal to 10 per cent of the weight of the ore, was then sprinkled over the ore pulp by straining through canvas or chamois and the stirring continued for 3 hr. longer—when amalgamation was completed.

The whole charge was then washed from the pan into a settling tank provided with radial arms and agitated under a constant flow of water until the amalgam collected in the bottom of the tank and the tailings were washed away. The amalgam was then transferred to a small pan known as the cleanup pan, where it was stirred with additional mercury and washed with water until free from ore particles. The silver and gold were finally recovered by retorting the amalgam.

The chemistry of this process is the same as that of the Patio process, except that the iron of the pan and mullers also acts as a reducing agent, not only for precipitating silver in metallic state from its chlorides but also for preventing the formation of any chlorides or sulphides of mercury, and in this manner avoids the chemical loss of mercury mentioned under the Patio process. The ore must be siliceous or neutral in character to avoid precipitation and the loss of effective copper salts by the carbonates of lime and magnesia, although the iron of the pan has a tendency to reduce these salts to copper and hence militate against their effectiveness.

Two important modifications of the process were developed later. The first was known as the Boss process, in which the ore from the stamp mill was finely ground in pans and then flowed continuously through a series of amalgamating pans and settling tanks. This made the process continuous and saved considerable time and labor in transferring the charges from settling tanks to pans and from pans to settling tanks. The other modification, where economic conditions were favorable, was the introduction of the chloridizing roast previous to pan amalgamation. By this means the silver sulphide minerals, as well as the base-metal sulphides, were converted more completely into the chlorides in the roasting furnace, and the addition of salt and copper sulphate to the pan was rendered unnecessary unless the ore was insufficiently chloridized during roasting.

The pan-amalgamation process was well adapted to surface or oxidized silver-gold ore where the gold was subsidiary in value and not amenable to ordinary amalgamation and where the silver occurred as a haloid, or, if it occurred as a sulphide mineral, the ore was comparatively free from the base-metal sulphides. With such ore the recovery averaged between 80 and 85 per cent; the process was metallurgically clean; it yielded a product of bullion and involved no troublesome by-products; it was simple to operate; the supplies needed were cheap and easily obtained.

The disadvantage of the process was the small capacity and consequent high operating cost per unit of equipment, *viz.*, one pan. This has been the principal reason for the abandonment of this process and its replacement by leaching processes, particularly the cyanide process. The last two notable and eminently successful examples

of the pan-amalgamation process in the United States were at the Commonwealth mine, Pearce, Ariz., and at the Presidio mine, Shafter, Tex.

At the Commonwealth mine the ore was almost pure quartz; the ore milled averaged 15 oz. silver per ton; the silver occurred principally as a halide. The gold was subsidiary in value and averaged 0.05 oz. per ton. The first mill, built in 1896, had a capacity of 200 tons daily, which was large for pan amalgamation. The ore was crushed dry in Jenisch ball mills, but these were not entirely satisfactory, and after a fire in 1900 they were replaced by stamps and the ore was crushed wet. The mill operated until 1910, when the cyanide process was introduced. The recovery by pan amalgamation was 77 per cent on 15-oz. ore; the average cost of milling was $1.60 per ton for the 400,000 tons treated; the loss of mercury was 0.2 lb. per ton of ore.

At the Presidio mine[1] the ore was a siliceous limestone averaging 18 oz. of silver per ton, principally as a chloride. The ore also contained some galena. A pan-amalgamation mill of 70 tons daily capacity was built in 1884 and operated continuously until 1913, when it was converted into a cyanide plant of larger capacity. The average recovery by pan amalgamation is reported to have been 85 per cent. So far as the writer knows, the reconstruction of this mill marked the extinction of the pan-amalgamation process in the United States, but the process is probably still used to some extent in South America.

CHLORIDIZING ROASTING AND LEACHING PROCESSES

Chloridizing Roasting.—The gradual exhaustion of oxidized ore and the increase of base-metal sulphide minerals with the silver sulphide minerals, together with the increased facilities for transporting fuel and supplies, led to the introduction of chloridizing roasting and the attendant leaching processes.

In chloridizing roasting, furnace heat replaces water in effecting the desired chemical reactions, *viz.*, that of breaking up the sulphides in the natural minerals and converting the metals into their respective chlorides. This is done by roasting the ore with common salt and a proportionate amount of sulphur in almost any type of roasting furnace. If too much sulphur is present in the ore, the excess is removed by preliminary roasting; if the ore is completely oxidized, sulphur is usually added in the form of pyrite or native sulphur in sufficient quantity to complete the reaction. The reaction between the salt and sulphur, when heated in the presence of air, is shown by the following equation:

$$2NaCl + S + 2O_2 = Na_2SO_4 + Cl_2 \qquad (1)$$

From this equation it is obvious that an excess of sulphur in an ore is an unnecessary consumer of salt.

For the metals that are converted into chlorides by chloridizing roasting, the following equations will indicate, in their simplest forms, the chemical reactions that occur in the furnace:

$$2NaCl + Ag_2S + 2O_2 = Na_2SO_4 + 2AgCl \qquad (2)$$
$$2NaCl + CuS + 2O_2 = Na_2SO_4 + CuCl_2 \qquad (3)$$
$$2NaCl + PbS + 2O_2 = Na_2SO_4 + PbCl_2 \qquad (4)$$
$$4NaCl + 2CuO + S_2 + O_2 = 2Na_2SO_4 + 2CuCl_2 \qquad (5)$$
$$4NaCl + 2PbO + S_2 + O_2 = 2Na_2SO_4 + 2PbCl_2 \qquad (6)$$

The equations for oxidized ore apply also to the carbonates, which decompose to the oxides on heating. Sulphates and silicates decompose salt by the direct interchange of the elements and radicals without the addition of sulphur.

[1] ADKINSON, HENRY M., The Silver Mine of Texas, *Eng. Mining Jour.*, Aug. 2, 1902, pp. 150–151.

Iron pyrite loses one atom of sulphur at low temperature, which assists in decomposing salt for the chloridization of oxidized ore, as indicated above. The ferrous sulphide formed by the loss of this atom of sulphur reacts with salt in the presence of air to form ferrous chloride in a manner similar to the other metals. This salt is probably oxidized to the ferric chloride *in transitu* to the oxide of iron, but in either state it decomposes at low temperature and becomes an active chloridizing agent for the other metals. Comparatively little chloride of iron is ever found in leaching solutions or in fumes from chloridizing roasting. The iron oxide thus freshly formed undoubtedly becomes an active catalytic agent and assists in the above-mentioned chemical reactions.

There are good reasons for believing that basic chlorides and double chlorides are also formed; these need not be speculated on here, but will be discussed under the Jenness process, page 548. Arsenic and antimony, which are frequently found in silver minerals, probably form combinations of this character. The method of calculation stated above has been found to be remarkably dependable in practice, but it must be remembered that, in roasting, there is a dry mixture of ore and salt, both of which are crushed to pass, on the average, a 0.75-mm. screen. It is, therefore, impossible to get the intimate contact between the salt and the mineral particles that is obtained from a solution of salt and finer grinding of the ore. For this reason, and on account of volatilization and mechanical losses, it has been found advisable, while maintaining the ratio between the salt and sulphur, to increase the proportions of both about 25 per cent in relation to the ore; also, for the reasons above mentioned, it is needless to say that these computations cannot be applied to a silver ore containing no chloridizable base metal, because the amount of salt necessary to combine with silver alone would be almost negligible and it would be difficult to bring about chemical reactions.

From Eq. (1) it will be observed that 116 parts by weight of salt combine with 32 parts by weight of sulphur, or, in practice, it may be said that the ratio of salt and sulphur is as 4:1. If sulphur occurs in the ore, this ratio will govern the amount of salt required for an efficient chloridization. The amount of sulphur that will yield the best results is that which will combine with chloridizable metals to form their normal sulphides. For example, as shown in Eq. (3), 65 parts by weight of copper combine with 32 parts by weight of sulphur to form normal copper sulphide, or a ratio of copper to sulphur as 2:1. Therefore, an ore containing 4 per cent copper would require 2 per cent sulphur and 8 per cent salt to yield the most efficient chloridization. By the same method of computation, a 7 per cent lead ore would require less than 1 per cent sulphur and 4 per cent salt for chloridizing roasting.

In the early days of chloridizing roasting there was a tendency to use higher percentages of salt than necessary. Later practice reduced this amount, and it now ranges from 5 to 15 per cent of the weight of the ore, depending somewhat on the amount of sulphur present. Ten per cent is usually the maximum required for all ore treated by this process, and for this amount of salt the sulphur should be as near as possible to 2.5 or 3 per cent.

In the chloridizing roasting of silver ores, the roasting furnace does little more than start chemical action. For example, the ore-salt mixture remains in a Stetefeldt furnace only a few seconds while dropping from the top to the bottom—a distance of about 40 ft.—against an updraft. The red-hot ore is drawn from the furnace and dumped into a "soaking pit," or bedded on a cooling floor to a depth of 3 or 4 ft., where it remains several days until cool. More than 50 per cent of the chloridization is done on the cooling floor.

The temperature of chloridizing roasting should not exceed 600°C., which is a low red heat. Above this temperature there is considerable loss of the metallic chlorides by

volatilization. Gangue materials and water vapor, as a rule, have little influence on chloridizing roasting at low temperature. Gargeu[1] states that aluminum silicates begin to decompose salt at 550°C. Spring[2] states that lead chloride begins to decompose in the presence of water vapor at 110°C. and even sodium and potassium chlorides are partially decomposed at 400°C. Bagdasarian[3] found that water vapor, diluted with air, decomposes zinc chloride at temperatures as low as 500°C. This phase of chloridizing roasting will be discussed under Chloride Volatilization Processes.

Practically all types of roasting furnaces have been used for chloridizing, *viz.*, hand reverberatory, Bruckner, White-Howell, Stetefeldt, McDougall, Edwards-Merton, Wedge, Herreshoff, and Holt-Dern.

The most satisfactory type of furnace yet developed for ordinary chloridizing roasting, and the one most universally used at the present time, is the Wedge or "multiple-hearth" furnace, in which the ore and salt mixture is fed at the top and raked from one hearth to the next by rabbles or plows attached to radial arms from a vertical central shaft. This furnace is usually made with five superimposed hearths 20 ft. in diameter. It is fired at the bottom hearth with wood, coal, oil, or gas from an attached firebox. The coal required is about 10 per cent of the ore charge, depending on the quality of the coal used and the amount of sulphur in the ore. The capacity of such a furnace is 80 tons of charge (ore and salt) per day, although with careful manipulation it has reached 100 tons per day.

The Edwards-Merton is less complicated in construction than the Wedge furnace. It requires no specially designed firebrick or tile. The mechanical parts are simple in construction and easily obtained. These are requisites in isolated districts (see Brine Leaching of Silver Ores, page 530).

The Holt-Dern furnace was applied to chloridizing silver ore at Tintic, Utah. It was a low shaft furnace, built of concrete, and provided with a rocking self-dumping grate for discharging the roasted ore. The furnace was filled with a moist mixture of pulverized ore, coal, and salt. A low air blast was applied to facilitate combustion. New ore mixture was charged at the top, while the chloridized ore was drawn intermittently from the bottom. The operation of the furnace will be further described under Brine Leaching of Silver Ores.

The Stetefeldt furnace went out of use with the passing of hyposulphite leaching in the United States, but in 1924 it was revived in modified form for oxidizing roasting of flotation concentrates; it also has merit as a chloridizing furnace, for which it was originally designed.[4] It is believed none are now in use in the United States.

Where higher temperatures are used, as in volatilization roasting, the modern development of the White-Howell furnace is the only type that has been found satisfactory. This is the regular cement kiln used for burning clinker. It is a cylinder 100 to 125 ft. long and lined with firebrick. It is fired directly with oil, producer gas, or powdered coal, at the discharge end.

Dust losses are negligible in chloridizing roasting, because as soon as the temperature is high enough to start the sulphur burning, which is below a red heat, chemical action begins and the roasting charge has the appearance and physical character

[1] Gargeu, A., *Compt. rend.*, Vol. 102, p. 1164, 1886; *Ann. chim. phys.*, (6), Vol. 10, p. 105, 1887; Bagdasarian, A. B., Influence of Certain Solids and Gases on the Chlorization Roast, *Eng. Mining Jour.-Press*, June 13, 1925, p. 963.

[2] Spring, W., *Berichte*, Vol. 18, p. 344–345, 1885; Bagdasarian, 963.

[3] Bagdasarian, *op. cit.*, p. 964.

[4] *Vanadiun Ores.*—The United States Vanadium Co. operates a plant at Rifle, Colo., for the treatment of siliceous vanadium ores (roscoelite?) found in the sandstone beds of that vicinity. The ore carries about 3.5 per cent vanadium oxide. It is roasted with salt at low temperature, and sodium vanadate is formed instead of vanadium chloride. The roasted ore is leached with water, and the V_2O_5 is precipitated from the solution by the addition of sulphuric acid. This high-grade precipitate is filtered off, washed, dried, and shipped to the ferroalloy plants in eastern United States.

of having been wet with water. Losses that may occur are due to the volatilization of metallic chlorides as fume at high temperatures, and not to mechanical loss as dust.

Following chloridizing roasting there are, necessarily, attendant processes for the recovery of the metals. These are described chronologically in the following paragraphs.

Pan Amalgamation.—For a long time the pan-amalgamation process was used to recover silver and gold from ore that had been chloridized by roasting. The process was the same as that used on raw ores, except that the addition of salt and copper sulphate to the ore in the pan was unnecessary unless the chloridizing roasting was poorly done. This process was gradually superseded by leaching processes, for reasons already stated.

Brine Leaching of Silver Ores.—The actual leaching of silver ore with brine, after chloridizing roasting, began with the Augustin process in Germany in 1843 and continued to be used in Hungary for the recovery of silver from matte up to 1893. Owing to the prevalent use of pan amalgamation—even for ore which had been chloridized by roasting—and the early introduction of hyposulphite leaching, brine leaching of silver ore did not make much progress in the United States. It was first successfully applied by D. W. Brunton at the Stewart mill in Georgetown, Colo., in 1876. Later, he operated this process at the Caribou mine in Boulder County, Colo., and, up to 1879, at the Silver Peak mine in Nevada. Brückner furnaces were used for chloridizing roasting. No effort was made to recover any base metal except the copper used in precipitating the silver from solution. The process was not revived for the commercial treatment of silver ore until 1911, when the Holt-Dern process[1] was developed at Park City, Utah, and reached commercial operation in 1914. In 1915 a plant was constructed at Silver City, Utah, by the Tintic Milling Co. This plant during its operation became essentially a pilot mill for a larger plant constructed by the Standard Reduction Co. at Harold, Utah, to treat the low-grade silver-lead ore from the Tintic Standard mine. The larger plant had a capacity of 200 tons per day and began operations in January, 1921.

The process[2] consisted of a chloridizing roast in a Holt-Dern furnace, followed by a percolating leach with a nearly saturated solution of common salt acidified with sulphuric acid. The silver was recovered by precipitation on cement copper, and the copper and lead by precipitation on detinned scrap iron.

The recovery of lead at the start was to be incidental, as it was at the pilot plant; but, stimulated by the higher prices for the metal during the early '20's, effort was made to improve the recovery—which was less than 50 per cent—and to treat ores containing a higher percentage of lead.

The average analysis of the ore treated during 1924 was: Au, 0.025 oz. per ton; Ag, 18.26 oz. per ton; Cu, 0.3; Pb, 5.0; SiO_2, 65.0; Fe, 10.0; CaO, 0.7; S, 3.0; and As, 0.7 per cent. It is essential that the lime content of the ore be low, the sulphur not to exceed 4 per cent, and the gold be negligible.

The ore mixture was made up as follows: The ore, with 8 to 10 per cent salt, was crushed to pass a 10-mesh screen (about 1.8 mm. opening). Fuel was added in the

[1] Holt, Theodore P., Chloridizing Leaching at Park City, *Trans. A.I.M.E.*, Vol. 40, pp. 183–197, 1914; Schmidt, F. S., Rejuvenating the Chloridizing Roast, *Mining Sci. Press*, Aug. 29, 1914, pp. 324–328; Scibird, George H., Park City Milling Co., *Eng. Mining Jour.*, Aug. 8, 1914, p. 254; Dern, G. H., The Mines Operating Co., Park City, Utah, *Eng. Mining Jour.*, Aug 8, 1914, p. 253; Kler, Glenn A., Chloridizing Blast Roasting and Leaching, *Eng. Mining Jour.*, Feb. 6, 1915, pp. 265–269, and Feb. 13, 1915, pp. 315–322; Holt, Theodore P., Chloride Roasting and Leaching, Tintic Milling Co., *Mining Sci. Press*, Apr. 24, 1920, pp. 603–604.

[2] Allen, H. P., and W. C. Madge, Chloridizing Mill of the Standard Reduction Co., *Trans. A.I.M.E.*, Sept. 1925; *Mining Met.*, August, 1925, p. 444; Parsons, A. B., The Tintic Standard Reduction Plant, *Eng. Mining Jour.-Press*, Aug. 22, 1925, p. 284; Oldright, G. L., Present Trend in Treatment of Complex Ores, *Mining Met.*, July, 1924, p. 348.

form of coal dust, usually between 1 and 2 per cent, depending on the amount of sulphur (as sulphide) in the ore. With 3 per cent sulphur, 1.5 per cent coal was used; as the sulphur changed the coal was varied, using the ratio of sulphur : coal = 1:0.65. Sulphur was maintained as near 3 per cent as possible; if the sulphur content fell below 2 per cent, the charge burned unevenly and lost heat rapidly during the recharging period; if it exceeded 4 per cent, the charge fused in the furnace, became troublesome to handle, and was poorly chloridized. Water was a necessary constituent of the charge for the purpose of agglomeration and forming a more porous ore bed. It was added in sufficient quantity to make the ore stick together when pressed in the hand. With a 10-mesh feed the water required amounted to about 7 per cent; too much water made a hard calcine; too little made roasting slow with a tendency to be "spotty." Water was supposed to assist in the chloridization by the formation of hydrochloric acid.

The feature of this process was the unusual type of chloridizing furnace which has been described at the beginning of this section. The Holt-Dern roasters consisted of a row of reinforced-concrete boxes, 7 × 9 × 5 ft. deep inside, set end to end; on the bottom were mechanically operated grates with hoppers underneath. Leading into the hoppers under the grates, was a pipe through which an air blast was supplied at 8 oz. pressure by a direct-connected Sturtevant fan. This arrangement helped to cool the roasted ore and heated the air blast. A common flue, through which the gases were drawn, ran the full length of the furnaces and connected with the absorption chamber for the recovery of acid, and thence to the stack.

The furnace was started with a layer of coal dust dampened with oil, spread over the grate, and ignited. This was followed with a special ore mixture, richer with coal than the charge. The air blast was turned on, and when this charge was burning properly the regular charge was added. At regular intervals the grate mechanism was set in motion and the charge was lowered in the furnace, so as to leave a bed of red-hot calcines, about 10 in. deep, on the grate to start the new charge burning. As the roasted ore was drawn from the furnace, new ore mixture was added at the top in 4.25-ton charges. The capacity of each furnace was about 25 tons of calcines per day. The temperature in the center of the roasting ore was supposed to be between 700 and 750°C. The furnace was operated with a cold top to prevent, as much as possible, loss by volatilization.

The hot chloridized ore was dropped from the hoppers into a concrete launder through which a stream of brine or "weak" mill solution flowed. This flushed the calcines into one of six concrete leaching vats. These vats were 28 ft. in diameter by 11 ft. deep inside, and had a filter bottom made up of crushed quartzite. Each vat held about 225 tons of calcines when filled within 8 or 10 in. of the top. After leveling the charge, leaching was started. The lixivium was drawn through 3-in. earthenware cocks into two concrete tanks of the same size as the leaching vats. The first, or richer part of this lixivium, was designated as "pregnant solution" and carried about 3 oz. silver and 14 lb. lead per ton; the subsequent lixivium, known as "weak solution," was discharged into the second tank and was used for sluicing calcines into the leaching vats.

The hot lixiviant obtained in the manner above described, containing an excess of salt and the soluble base-metal chlorides derived from the chloridizing roast, formed a quick solvent for the silver chloride and some of the lead salts in the ore. It was necessary to maintain a slight acidity (varying from 2 to 5 lb. of acid to the ton) in the leaching solutions at all times. A small part of the supply was derived from the gas-scrubbing chamber through which the gases from the roasting furnaces passed, but it was necessary to maintain the greater part of this acidity by the direct addition of 66°Bé. sulphuric acid. The water from the scrubbing chamber probably contained

a mixture of sulphuric, sulphurous, and hydrochloric acids. The regular lixivium from the leaching vats contained about 22 per cent salt and had an average temperature of 62°C.

The time cycle for leaching the chloridized ore was as follows: filling the vats, 24 hr.; leaching with weak solution, 48 hr.; with barren solution, 48 hr.; with wash water, 8 hr.; draining, 2 hr.; emptying vats, 8 hr.

The presence of lime and magnesia was objectionable in an ore because they combined with the sulphur and prevented chloridization in the roasting furnace; they consumed acid in the leaching solutions; and they had a precipitating action on the base-metal chlorides. Gold in the ore was only slightly chloridized, and the recovery never exceeded 35 per cent. Gold, therefore, was not desired; if it occurred in the ore in appreciable quantity it was recovered from the tailings by another process. Chlorine gas added to the leaching solutions gave a good extraction of the gold, but it has not been found feasible to use this in practice. The recovery of gold will be further discussed under Chloride Volatilization Processes and Wet Chlorine-gas Processes.

A lixiviant saturated with salt was found troublesome to handle in commercial practice, and it apparently did not have the solvent power for silver chloride that was obtained by slightly weaker solutions. The mill solution, as finally constituted at the Standard plant, had a carrying capacity of 25 to 30 oz. silver per ton, which was a concentration not approached in practice. Dissolution of the lead, however, was quite a different problem. Lead in the calcines was considered as present in the form of the sulphate and not as the chloride. The quantity of lead salts that brine will carry depends on the solution temperature, the chlorine concentration, and the sulphate content. An equilibrium in the sulphate content was soon established in mill solutions, which prevented further dissolution of lead salts. If the sulphate content (expressed as Na_2SO_4) could have been kept below 2 per cent in the mill solutions of the Standard plant, it would have been possible to recover about 1.25 tons additional lead per day; but, as these solutions were returned to the circuit, the sulphate content was constantly increased by the addition of acid, and by the sulphates from new calcines. All known methods for removing these sulphates were prohibitive on account of the expense. Increasing the leaching time from 4 days to 9 days raised the recovery of the lead from 65.7 per cent to 92.5 per cent, but this procedure required greatly increased leaching capacity.

The silver was originally recovered from solution by precipitating on copper plates and was melted into bullion 975 fine. Later, the silver (and gold) were precipitated by cement copper (produced by the process) passed countercurrently to the lixivium through four Pachuca agitators. These tanks were made of concrete, and the agitation was done with compressed air. After a certain period the copper in the first agitator ceased to function; this was attributed to the deposition of metallic arsenic. The silver precipitate was then withdrawn from the first agitator, and the copper from the second agitator was by-passed into the first. The average analysis of the silver precipitate was: Ag, 8750 oz. per ton (30 per cent); Cu, 15; Pb, 2; As, 25; Sb, 1.5 per cent, and the remainder was principally iron, alumina, and "insoluble." This precipitate was washed and roasted slowly in a small reverberatory furnace. The arsenic was volatilized and recovered in bags as As_2O_3; the temperature was then raised to oxidize the copper. The roasted material was treated with hot dilute sulphuric acid (25 per cent), which dissolved the copper. The residue was dried and sold to the smelting companies. The analysis of the final silver product was: Ag, 10,000 to 14,000 oz. per ton; Cu, 1.0; As, 0.75; and Pb, 1.8 per cent.

The lixivium leaving the Pachuca agitators flowed through eight precipitating boxes or launders for the recovery of the copper. These boxes were 30 ft. long, 5 ft.

wide, and increased from 18 in. to 3 ft. in depth; they were made of concrete in the usual form, the bottoms sloping to facilitate sluicing. Ordinary scrap iron was first used as a precipitant, but later detinned sheet scrap was used in order to supply greater precipitating surface and to produce a higher grade copper precipitate. At comparatively low temperatures, the copper was precipitated preferentially from the lead. Part of the cement copper thus produced was used to precipitate the silver, and the balance was shipped to the smelters; it contained about 100 oz. Ag per ton, 50 per cent Cu, and 6 per cent Pb, besides iron and other impurities.

The lead also was precipitated on detinned scrap sheet iron, but, to get a sufficiently rapid action, the temperature of the solution had to be maintained above 75°C. The solution leaving the copper precipitating boxes had a temperature of about 45°C; this was pumped into a tank fitted with copper coils and was heated with low-pressure steam to the required temperature before going to the lead precipitating boxes. There were 15 lead precipitating boxes of the same size and form as the copper precipitating boxes. The lead precipitate contained 6.5 oz. Ag per ton, 70 per cent Pb, and 5 per cent Cu, besides iron, alumina, and other impurities; it was shipped to the smelters without drying and contained 21 per cent moisture. The iron and the alumina in the copper and the lead products were probably in the form of basic salts.

It was found advantageous to remove the tin from the tin-plate scrap before using the iron as a precipitant. This was accomplished by treating the scrap with a solution of caustic soda containing a small amount of litharge.[1] The litharge was obtained by roasting the lead precipitate. The tin was not recovered.

The average recovery of the metals from the ore in 1925 was gold, none; silver, 89.8 per cent; lead, 65.7 per cent; copper, 52.2 per cent.

The cost of mill treatment per ton of dry crude ore was: operating labor, $1.738; operating supplies, $1.319; repair labor, $0.553; repair supplies, $0.539; power, $0.283; total, $4.432. The cost of labor and supplies at the plant was: labor, $5 per 8-hr. day; salt, $4; slack coal, $3.05; and tin-plate scrap, $18 per ton.

The concrete construction used in the leaching vats, precipitating boxes, and tanks was important. The aggregate was composed of crushed quartzite and siliceous sand containing 96 per cent SiO_2. The maximum size of the aggregate was 1.5 in.; the proportions used were 65 per cent of the coarse and 35 per cent of the fine. The ratio of cement to aggregate varied from 1:3 to 1:4, except in the lead- and copper-precipitating boxes where a ratio of 1:5 was used. None of this concrete showed any deterioration from the corrosive solutions except the walls of the absorption chamber, where the gases from the roasting furnaces were sprayed; these walls were attacked by the acids and were then protected by plank, painted with elaterite. Cracks occasionally developed in the lead-precipitating boxes owing to the change in temperature when washed with cold water; such cracks were chipped out and filled with a 1:1 cement mortar.

The mill was placed on a steep hillside, and the solutions were moved by gravity as much as possible; where pumping was necessary, wooden air-lift pumps were used for the corrosive solutions, and acidproof centrifugal pumps handled the barren solution. The launders were made of concrete.

Considerable space is devoted here to the description of this plant because it represented years of experimentation and the expenditure of a large amount of money in an effort to exploit a new principle of ore roasting on an old metallurgical process; brine leaching of silver-lead ore was studied here also in great detail under the most favorable conditions. The results as a whole show that little, if any, pecuniary advantage was gained over shipping the ore to the local smelters; this fact does not reflect adversely on the merit of the brine-leaching process, but clearly illustrates how

[1] SCHNABEL, CARL, "Handbook of Metallurgy," Vol. 2, p. 423, New York and London, 1898.

local conditions not only should govern the selection of an ore-treatment process, but may affect its commercial value.

The interesting and novel features of the plant were the roasting furnaces and the use of concrete construction. The basis of success in chloridizing roasting and leaching processes is an efficient chloridization; consequently, the interest in this plant centers primarily in the furnaces used for chloridizing roasting.

Whatever economies may have been obtained in the construction and operation of the Holt-Dern furnace, it was fundamentally wrong for chloridizing roasting. Highly oxidizing conditions are imperative for efficient chloridization; these conditions cannot be obtained when carbonaceous material is mixed with the ore charge and used as fuel. The reducing conditions in this furnace are amply proved by the tendency of the ore to matte or fuse when the sulphur content exceeds 4 per cent. At the low temperature maintained, the effective chlorine can be liberated from the salt only by the sulphuric acid radical; the sulphuric acid radical can be formed only by supplying the elemental sulphur with sufficient oxygen. Apparently, to obtain these essential oxidizing conditions, it would be better to use a percentage of sulphur high enough to maintain the heat of chemical reaction and use no coal at all. It is necessary also, in the operation of these furnaces, to use an ore charge too coarse for efficient chloridization, in order to maintain sufficient draft; unless the mineral particles are freed from the gangue by the coarse crushing, it is impossible to chloridize a mineral particle entirely enveloped by gangue. The ore mixture should be crushed to pass a 20- or 30-mesh screen for proper chloridizing roasting.

Water cannot possibly have any chemical influence on the chloridization at the temperature and under the conditions existing in this furnace; it is completely evaporated before any decomposition can take place. The water probably dissolved some salt and thereby brought that salt into more intimate contact with the mineral particles, and, in this manner, aided the chemical action. Aside from improving the physical condition of the ore charge, it could only consume the extra heat units necessary for its evaporation.

The chloridization might be improved if the roasted ore had been allowed to remain on a cooling floor for a few days, but this, of course, would lose the heat desired for the leaching solutions. Probably much of the chloridization is accomplished by the base-metal chlorides formed by the reaction of their sulphates with the salt.

Comparing the results obtained at the Standard plant with those obtained by hyposulphite leaching on the much more difficult ores from Aspen, Colo. (see Hyposulphite Leaching of Silver Ores), the question arises whether chloridizing roasting in a standard furnace and under proper conditions, followed by hyposulphite leaching, would not give much better results; such treatment of ore from Creede, Colo., which is similar in character to the Tintic ore, yielded a recovery of over 90 per cent of the silver. Lead and copper are recovered also by this process. The final products obtained are fully as high grade and are marketed in the same manner as the products obtained at the Standard plant. Hyposulphite solutions are noncorrosive and are easily regenerated.

Losses by volatilization at low-temperature roasting in a standard chloridizing furnace are not prohibitive, and the volatile chlorides are easily recovered.

Pilot plants, including Holt-Dern furnaces to be followed by brine leaching, were installed at San Vicente, Bolivia, and at Pulacayo, Bolivia, to replace the hyposulphite leaching that has been in use there for 30 years. The success of this process hinged on the adaptation of blast-roasting to high sulphur ore. An attempt was made to solve this problem by returning a portion of the calcine to the charge bin to be mixed with the crude ore, thereby reducing the sulphide-sulphur content of the furnace

charge.[1] The editor attempted to learn some of the detailed results of these plants, but without success. It is interesting to note, however, that there was some talk about constructing Holt-Dern plants in Bolivia under Board of Economic Warfare auspices as late as 1942–1943.

Manganese-silver Ores.—Clevenger and Caron[2] have made an exhaustive study of the treatment of manganese-silver ores, which are notoriously refractory. The results of this work may be summarized as follows:

"It appears that in manganese-silver ores of secondary origin, formed at low temperature, the refractory silver mineral is manganite of silver; whereas, if the ore deposition has taken place at higher temperature, silver silicate may also be present."

"Our experience, however, is that, whether or not the manganese present has a fixed ratio to the silver, it is necessary to dissolve all of the manganese; or if reduction is practiced, all the higher oxides must be reduced to manganous oxide in order to obtain the highest recovery of silver. This clearly indicates that in certain of these ores although the silver has no fixed ratio to the manganese, the manganese is directly related to the refractory silver. . . . We have found that the refractory silver in the original ore is insoluble in all the common solvents for metallic silver and its salts—that is, cyanide solutions of all concentrations, dilute and concentrated nitric acid, dilute sulphuric acid, salt solution, alkaline thiosulphates, ammonia, mercury, and other reagents. This conclusion harmonizes with all previous work on the problem.

"In the chloridizing roast, as formerly carried out in various types of roasting furnaces, the ore was first given an oxidizing roast, which was followed by the addition of the sodium chloride for chloridizing. During the oxidizing roast the MnO_2 would be dissociated with the formation of the lower oxides Mn_2O_3 or Mn_3O_4, depending upon the temperature and time of heating. Also, during this stage, a large portion of the amenable silver compounds in the ore would combine with the Mn and SiO_2 to form additional refractory compounds. It is, therefore, not unusual during an oxidizing roast of ores of this class for all of the silver to be converted into refractory compounds where originally there had been only 60 to 75 per cent of refractory silver. On the addition of sodium chloride to the heated ore in an oxidizing atmosphere a considerable proportion of the silver is converted into silver chloride, but the conversion is never complete, as indicated by the subsequent low recovery of silver. It is, therefore, obvious that the conversion would probably be more complete if oxidation could be avoided during the earlier stages of roasting.

"With chloridizing blast roasting, the necessary fuel and salt are mixed directly with the ore, and, after ignition, the air is either blown or drawn through the charge. Under these conditions, during the heating of the ore an excess of carbon is left which to a greater or less extent reduces the higher oxides of manganese to the lower oxides, even as low as manganous oxide. This condition largely liberates the silver in a finely divided metallic condition which is ideal for chloridization. However, during this first stage, in which the conditions are reducing, no chloridization of the silver can take place at the temperature employed; but later, after the fuel is consumed, the mixture of hot ore and sodium chloride comes in contact with the air, at once giving conditions favorable to chloridization."

This idea has been developed in the Vermaes process[3] in which the finely crushed ore is mixed with organic material and sodium chloride. This mixture is heated to a temperature of 320 to 330°C., after which the ore is cyanided. The organic matter is

[1] Ferron, Robert D., Blast-Roasting an Improvement over Old Patera Process in Bolivia, *Eng. Mining Jour.-Press*, Nov. 29, 1924, p. 854.

[2] Clevenger, Galen H., and Martinus H. Caron, The Treatment of Manganese-silver Ores, *U. S. Bur. Mines Bull.* 226, 1925.

[3] Vermaes, Stefanus Johannes, Treatment of Refractory Manganese Ores Containing Precious Metals or Silver Alone, U. S. patent 1234426, July 24, 1917; Clevenger and Caron, *op. cit.*, p. 34.

added for the purpose of breaking up the manganese-silver compounds. The reduction of natural manganese dioxide begins at a temperature of approximately 90°C. in an atmosphere of hydrogen or carbon monoxide. In the dry distillation of organic material, hydrogen, carbon monoxide, and hydrocarbons are readily formed at temperatures of 180 to 200°C., and the reducing gases so formed will react with the higher oxides of manganese, reducing them to a lower oxide—generally to Mn_3O_4. According to Vermaes, the silver will then combine with the salt to form silver chloride. Since the temperature in this process does not rise above 330°C., all the charcoal resulting from the distillation of the organic material remains unacted upon and finely divided throughout the ore. Vermaes claims there is no loss of gold or silver by volatilization at this low temperature. Clevenger and Caron found a small loss of gold but no loss of silver when conducting the chloridizing roast in a reducing atmosphere at 300°C.; they also found that "the silver is not all present as chloride, a small part being in the metallic state, since decomposition of silver chloride begins in a reducing atmosphere at 300°C." The amount of salt used in this process is 1 to 3 per cent depending on the proportion of silver present in the ore.

The percentage of silver volatilized[1] from manganese-silver ores by the chloride volatilization process is far below that which would be necessary for successful commercial operations.

Conversion of these refractory manganese-silver compounds into silver chloride by wet methods has been attempted by several investigators, but chiefly by Linton.[2] He ground the ore and salt to pass a 100-mesh screen and then agitated the mixture for 24 hr. in a 5 per cent solution of sulphuric acid. The ore pulp was then filtered off, washed, and cyanided. The silver recoveries varied from 60 to 94 per cent. Clevenger and Caron found that the extraction of silver varies as the manganese is dissolved as sulphate, and in order to obtain a high extraction of silver it is necessary to dissolve all the manganese; therefore, the process is amenable only to ores low in manganese and with a gangue insoluble in acid. The use of hydrochloric acid instead of sulphuric acid has yielded high recoveries of silver when followed by cyanidation; free chlorine is evolved when either acid is used. It is difficult, particularly with the higher grades of manganese-silver ores, to filter and completely wash the ore pulp. The manganese sulphate remaining in the residue is an active cyanicide.

Brine Leaching of Lead Ores.[3]—In 1916 considerable work was done on the hydrometallurgy of lead at the Bunker Hill & Sullivan mine at Kellogg, Idaho, following an attempt to use the dry chlorine-gas process. It was found that dry chlorine gas, acting on lead sulphide, produced lead sulphate and not lead chloride. The fine galena concentrates were, therefore, roasted to the sulphate of lead by the ordinary method, and the roasted ore was leached with a strong solution of common salt. This solution was electrolyzed, using sheet-iron anodes. Pure lead was obtained in spongy form with the theoretical consumption of iron. The process seemed feasible with reference to cost and recovery, but, with a smelting plant already in operation and treating all classes of ore, the leaching process was not developed to a commercial scale.

Experimentation by U. C. Tainton, metallurgical engineer for the Bunker Hill & Sullivan Co., was continued in perfecting the electrolytic cell, and a pilot plant was constructed to treat the tailings from the concentrating mill. The tailings contain

[1] CLEVENGER and CARON, *op. cit.*, p. 31.
[2] LINTON, ROBERT, Silver Ore Treatment in Mexico, *Jour. Chem. Met. Soc. of South Africa*, Vol. 9, p. 307, March, 1909; CLEVENGER and CARON, *op. cit.*, p. 31.
[3] LYON, D. A., and O. C. RALSTON, Innovations in the Metallurgy of Lead, *U. S. Bur. Mines Bull.* 157; Leaching Lead from Carbonate Ores, *Mining Sci. Press*, Mar. 1, 1919, pp. 277–282; RALSTON, O. C., Salt in the Metallurgy of Lead, *Trans. A.I.M.E.*, Vol. 57, pp. 634–656, 1917.

considerable siderite or carbonate of iron. They were given an ordinary oxidizing roast to convert the iron into the insoluble oxide and the galena into the sulphate. The calcines were then leached with hot brine containing ferric chloride. The lixivium was passed through a diaphragm electrolytic cell equipped with insoluble anodes. Lead and silver were precipitated on the cathodes, and the chlorine liberated at the anodes was absorbed by the ferrous chloride in solution, regenerating ferric chloride for new lixiviant.

Later development in this pilot plant during 1924–1925 resulted in further changes in the process. The ore was roasted at a temperature not exceeding 500°C. in a cylindrical furnace, which was heated electrically by a central core of heat-resisting iron pipe; this obtained a highly oxidizing atmosphere without the contamination of fuel gases.

The roasted ore was leached with water to remove the zinc and other soluble sulphates. It was then leached with hot brine from the electrolytic cells, to which some bleaching power had been added. The calcium chloride in the bleaching powder precipitated the sulphuric acid radical from solution as calcium sulphate and thereby obtained an efficient dissolution of the lead. This was followed by a leach with new solution. The ore treated contained about 5 per cent lead. The consumption of salt was 30 to 50 lb. per ton of ore.

The lixivium from the leaching vats contained 12 to 15 lb. of lead per ton and was sent to the electrolytic cells; these cells were closed for the recovery of the chlorine. The anodes were graphite and were separated from the cathodes by diaphragms. The liberated chlorine gas was passed over lime to prevent it from becoming obnoxious around the plant; this also formed the bleaching powder used in the process. Only the calcium chloride—not the calcium hypochlorite—thus produced performs any valuable function in the process. The lead was precipitated on a submerged revolving cathode (135 r.p.m.) with a current density of 15 amp. per sq. ft. and at a pressure of 3 to 4 volts. The lead deposited in a spongy condition and was constantly brushed off the cathode. It was pumped from the bottom of the cells and sent to a filter to separate it from the electrolyte. The lead sponge was melted into bullion, and the electrolyte, entirely free from lead, returned to the leaching vats. Gold and silver were deposited with the lead, but, by using a lower current density, it was possible to precipitate them preferentially from the lead in a highly concentrated product.

The Chemical & Metallurgical Corp. of England likewise developed the *Elmore process* for the extraction of lead and silver from lead-zinc concentrates or high-grade complex ores. The ore was given a chloridizing roast with a small amount of salt at a temperature not exceeding 400°C., in order to chloridize the silver only. The roasted ore was than agitated in a series of rubber-lined cones with a saturated salt solution containing 10 per cent sulphuric acid, at a temperature of 100°C. Sulphureted hydrogen was given off, and lead sulphate was formed. Sulphur dioxide gas was introduced into the last cone to prevent the formation of silver sulphide from the zinc sulphide present. Lead and silver passed into solution, and the zinc remained as a sulphide with the gangue. The solution was passed over lead plates to precipitate the silver and then cooled to precipitate the lead as sulphate and chloride. The process was not a commercial success on account of the extreme mechanical difficulty in handling the hot corrosive acid solutions on a large scale.

The Combined Metals Reduction Co.,[1] an organization financed by the National Lead Co., erected a plant at Bauer, Utah, in 1925, to treat complex sulphide ores by the Snyder-Christensen process.[2] The ore treated was very complex middling from

[1] Snyder-Christensen Process Works Well at Bauer, Utah, *Eng. Mining Jour.-Press* July 4, 1925, news item.

[2] U. S. patent 1549062, Aug. 11, 1925, N. C. Christensen.

the concentrating mill where selective flotation was used on complex ores. This middling product was treated with hot brine acidified with hydrochloric acid, which dissolved the lead and silver sulphides (also oxidized minerals) but did not attack the zinc and copper sulphides. Hydrogen sulphide was evolved which might be used as a precipitant for the silver and lead if desired, but was sent out of the stack in the Bauer operations. It was found more advantageous to separate the lead chloride by cooling the lixivium than to recover the lead direct from this solution by means of electrolysis or by precipitating on iron. An attempt was made to fuse the lead chloride thus produced and precipitate the lead by the addition of metallic zinc, but no market could be found for the zinc chloride. It was later proposed to smelt the lead chloride with lime and return the calcium chloride to the circuit.

The hydrochloric acid used for acidifying the brine was made in a separate plant so that the sulphates could be eliminated from the lixiviant and thereby secure a high extraction of the lead (compare with the Holt-Dern process described under Brine Leaching of Silver Ores). The lixiviant was a nearly saturated solution of salt; the acidity was varied to satisfy the lead content of the ore treated and was maintained at the ratio of 0.5 lb. hydrochloric acid to each 1.0 lb. of lead in the ore; at the end of the leaching operation, the lixiviant should contain 0.5 per cent of free hydrochloric acid. During the leaching operations it was necessary to maintain the temperature of the lixiviant at 95°C., which was near the boiling point. Such a solution is very destructive to any type of leaching vat and to all appliances used in the plant; the materials used in this construction were confined to wood and rubber. The lixivium coming from the leaching vats was said to carry 4 per cent or 80 lb. lead per ton.

The plant was designed for a capacity of 150 to 200 tons of ore per day, but the mechanical difficulties in handling the hot corrosive acid brine, in disposing of large quantities of hydrogen sulphide gas, and in making a satisfactory recovery of the metals were so great that the process did not pass the pilot-plant stage.

An experimental leaching plant, using practically the same process, was established at Keeler, Calif., by the Chemical Development & Reduction Co.[1] The extraction of silver and copper was about 90 per cent.

Brine Leaching of Copper Ores.—The use of chlorine in the metallurgy of copper is now confined to the chloridizing roasting of cupriferous cinder from sulphuric acid manufacture. The principal source of this material is pyrite from Spain, which is not only shipped to the United States but to many points in Europe, although other sources of pyrite are also used in quantity.

The practice is essentially the same in the United States and Europe, and also in Japan. The process is more extensively used in Europe and some modifications were introduced there by Ramên[2] that are known as the Ramênia system. The acid roasters are operated so as to leave a little more sulphur than copper in the cinder The average copper content is between 2.5 and 3 per cent, and the sulphur is between 3 and 4 per cent. This slight excess of sulphur is desired to get the proper heat of reaction. If not already in fine condition, the cinder or calcine from the acid roasting furnaces is pulverized to pass a 10-mesh screen. For this grade of cinder, 8 to 10 per cent of salt is added. The Scandinavian plants use principally Norwegian pyrite cinders, and these vary widely in both chemical and physical properties. Some of them contain 2 to 6 per cent zinc. The zinc sulphide does not oxidize readily, and consequently the cinder carries a higher percentage of sulphur, which must be compensated with an additional percentage of salt.

[1] Dawson, C. M., The Experimental Plant of the Chemical Development & Reduction Co., *Eng. Mining Jour.-Press*, Sept. 5, 1925, p. 383.

[2] Ostman, N., Chloridizing and Leaching as Practiced in Sweden, *Eng. Mining-Jour.*, Mar. 5, 1921, pp. 417–422.

The furnaces used are the Wedge type in the United States and the Ramên-Beskow type in Europe. Both types are multiple-hearth furnaces and are usually direct-fired on the lower hearth by producer gas or by coal from a firebox.

The Wedge furnace is 20 ft. in diameter and has five hearths. The Ramên-Beskow furnace is essentially of the same construction as the Wedge, but the first and second hearths are separated, making two compartments of the furnace. The combustion gases thus are kept separate from the acid gases from the chloridizing roast. The draft is regulated by fans. The ore mixture on the first hearth is brought to a temperature of about 300°C. by the use of fuel; this is sufficient to start the chloridizing action. From this point the ore passes to the lower hearths successively, and, with the chemical action started, enough heat is generated exothermically to complete the chloridization without extraneous fuel, and there is no danger from overheating or from loss by volatilization.

The coal required in American practice varies from 8 to 12 per cent of the weight of the cinder, depending on the character of the cinder treated, the furnace conditions, and the quality of coal used. At the Oscarshamn Copper Works, Oscarshamn, Sweden, where the latest improvements of the Ramênia system have been in operation over twenty years, the Ramên-Beskow furnaces are fired with producer gas made from tarry wood. The wood consumed corresponds to about 2 per cent of coal, based on the weight of the cinder. In order to maintain the heat of reaction, they mix a certain amount of green pyrite with the cinder during chloridizing roasting. Since they pay for the sulphur and copper, and sometimes for the iron in cupriferous pyrite, the amount paid for the sulphur thus consumed as fuel makes their actual fuel cost equivalent to American practice, although it is not so published.[1] The temperature is never allowed to exceed 1100°F., or 600°C. Below this temperature there is no loss of copper by volatilization.

The leaching vats are made of wood. Concrete, glazed tile, and acidproof brick have been used for lining vats in the United States, but operation over a period of years has proved that wood is as satisfactory material as any other. In Europe, reinforced concrete is used. Connecting pipes or launders are made of wood, and solutions are usually lifted by air-lift pumps, although in Europe wooden centrifugal pumps have proved satisfactory after long service. The filters are built of strips of wood in the form of lattice work. These are covered with prairie grass or similar material, and on top of this is placed several inches of wet leached cinder.

In American practice, the hot ore from the roasting furnaces is dumped directly into the vats. Some plants in Scandinavia experienced considerable trouble with hard lumps forming in the chloridized ore, due to the formation of anhydrous sodium sulphate. Ramên overcame this difficulty by designing a "preleaching machine," in which a thin layer of the hot chloridized ore from the roasting furnaces is evenly sprayed with sufficient water to permit the crystallization of the sodium sulphate, and the moistened ore then remains in a pulverulent condition. This machine runs continuously, and the preleached ore is conveyed to storage bins, where it is picked up by a grab bucket and placed in the leaching vats. Considerable steam is generated by this operation, which is condensed and furnishes hot water for leaching.

The gases from the chloridizing roasting furnaces pass through scrubbing towers. These are built of wood on a brick or concrete base. They are loosely filled with any inert material and sprayed with water at the top. They prevent the noxious gases

[1] Coincident with this development may be mentioned a modified construction of the Wedge furnace for autogenous blende roasting. It is 25 ft. in diameter and has eight hearths. The essential feature of the furnace is the arrangement for by-passing the roasted ore between the several hearths in order to obtain a desired distribution of the ore, preheated in the upper part of the furnace, among the lower reaction chambers. INGALLS, W. R., *Mining Met.*, December, 1922.

from escaping into the atmosphere and becoming a nuisance; they also condense and recover the acid fumes. The hot acid water from these towers is used for leaching purposes. In the Ramênia process the acidity of this water is kept at 15 to 24 g. of HCl per liter, which ensures the extraction of all soluble copper.

The leaching vats can be made any size, but usually hold about 100 tons. The ore bed is 3 to 4 ft. deep. By utilizing the hot ore, hot acid water from the scrubbing towers, and hot water from other sources mentioned, all leaching is done with hot solutions which average between 30 and 40°C. on leaving the vats and contain about 25 g. of copper per liter.

In Europe, the time of leaching ranges from 35 to 45 hr. under the ordinary system, but by using a "preleaching" machine this is reduced to about 24 hr. In America, where the copper extraction is usually made by the acid makers, the acid roasting furnaces are better controlled and the cinder is in better physical condition for chloridizing roasting. Under these favorable conditions leaching can be completed in less than 10 hr. in the ordinary manner, and even with unfavorable conditions the time seldom exceeds 24 to 36 hr. After washing, the cinder is removed from the vats by grab buckets, or by other means, depending on local conditions. The copper remaining in the leached cinder is not over 0.1 per cent and is usually less than that. This gives an average extraction of about 97 per cent.

The copper is recovered from solution by precipitation on scrap iron. This is done in the usual "boxes" or launders, which yield a precipitate containing about 70 per cent copper, or in "tumbling barrels" or drums which yield a precipitate containing 85 to 90 per cent copper. The advantage of the revolving drum is that the precipitation is done quickly by agitation, and the iron is kept clean, so there are no basic iron salts formed to contaminate the copper precipitate.

The leached cinder is known as purple ore, or "blue billy." If the original pyrite was commercially pure, the purple ore contains 55 to 68 per cent Fe, and not over 0.01 per cent P, 0.2 per cent S, and 0.1 per cent Cu. In 1891, Bird, of England, discovered that this material could be pressed and burnt into strong briquettes without any binder. This idea was developed commercially for fine iron ores, first by Anderson in America in 1888, and later by Gröndal in Sweden in 1896. The purple ore is pressed by slow compression into briquettes and heated in tunnel furnaces to a temperature of 1450°C. At this temperature practically all the sulphur is removed and the briquette is sintered. In this condition it makes a desirable iron ore, which assures a saving of 8 per cent coke in the blast furnace and frequently increases the capacity 30 per cent compared with ordinary iron ore. It is extensively used in Europe and Japan.

Under the circumstances it is difficult to arrive at the actual average cost of producing copper by this process, since the recovery of copper is only one of three phases in the treatment of the original pyrite. In America, the copper-recovery plant is an adjunct to the acid plant. The purple ore is nodulized and sold to the iron smelters. The profits derived from the copper and iron may be deducted from the cost of acid making. In Europe, the cupriferous cinder is bought from the acid maker, and the recovery of the copper is expected to pay all the expenses of producing a desirable iron-ore briquette, which is sold to the iron smelter. A disadvantage of copper recovery by leaching ores that have been given a chloridizing roast is that the spent solutions are highly corrosive and are destructive to fish. A technically successful plant at Garwood, N. J., operating on pyrite cinder, had to shut down because of contamination of the stream into which its solutions flowed.

Brine Leaching of Zinc Ore.—Chloridizing roasting and water or brine leaching, as described for copper ore, have been successfully applied to zinciferous cinder within the last few years for the purpose of extracting zinc in solution for

the manufacture of lithopone.[1] The treatment of zinc ores will be further discussed under dry chlorine-gas processes.

Hyposulphite Leaching of Silver Ores.—Hyposulphite (sodium thiosulphate) leaching came rapidly into favor in the United States after 1885; it was already well established in Mexico. It reached the zenith of its popularity between 1886 and 1893 and was practically abandoned as a metallurgical process at the end of that period, owing to the demonetization of silver in the United States and the general closing down of silver mines. The process is still used to a limited extent in South America and Mexico.

Chloridizing roasting necessarily precedes the leaching, and the chloridized ore is washed with water to remove the base-metal chlorides before applying the hyposulphite solution. This process is, therefore, closely related to brine leaching. It is essentially a process for silver ores, and the base metals are considered a nuisance. Silver is recovered as a sulphide from the hyposulphite solution by precipitating with sodium sulphide and the hyposulphite is thereby regenerated.

When the chloridization of the silver is low, because of inefficient roasting, the extraction is low. Zinc sulphide acts in an unexpected manner. At the Holden Lixiviation Works in Aspen, Colo., the ores carried about 2 per cent zinc, and a zinciferous pyrite was used as a source of sulphur. The short period of roasting in the Stetefeldt furnace and 4 days of heap roasting on the cooling floor did not oxidize the zinc sulphide, although the chloridization of silver was satisfactory. As soon as the chloridized ore was placed in the vats and leached with water, 20 to 40 per cent of the silver reverted to the sulphide, owing to precipitation by the unoxidized zinc sulphide in the ore.[2] By roasting with a clean pyrite, this difficulty was largely removed.

These defects in hyposulphite leaching were overcome to some extent by E. H. Russell,[3] who discovered that a little copper sulphate added to the hyposulphite solution formed a double salt of sodium cuprous thiosulphate, having the formula

$$4Na_2S_2O_3.3Cu_2S_2O_3 + xH_2O$$

This salt has the power of dissolving sulphide of silver by forming sodium silver thiosulphate and cuprous sulphide.

The solution thus formed is known in the Russell process as "extra" solution and follows the "regular" or "ordinary" hyposulphite solution in the leaching operations. By the use of this solution the extraction is restored to the extent of the original chloridization of the silver and even beyond that point.

The three lixiviants used in the Russell process are, therefore, (1) wash water (brine), to remove the soluble salts; (2) "regular' 'solution of sodium thiosulphate; (3) "extra" solution of sodium cuprous thiosulphate.

The ore treated by the Russell process at Aspen, Colo.,[4] in 1891–1893, affords a good example of a troublesome ore to treat by hyposulphite leaching. It had the following composition:

Ag, 27.92 oz. per ton; Pb, 2.28; SiO_2, 21.66; $BaSO_4$, 20.92; CaO, 11.00; MgO, 4.24; Fe, 10.02; Zn, 2.85; Cu, 0.16; S, 8.10 per cent.

[1] OSTMAN, *op. cit.*, p. 421.

[2] MORSE, W. S., The Effect of Washing with Water upon the Silver Chloride in Roasted Ore, *Trans. A.I.M.E.*, Vol. 25, pp. 587–594, 1895.

[3] STETEFELDT, C. A., Working of Silver Ores by the Leaching Process, *Trans. A.I.M.E.*, Vol. 12, pp. 291–295, 1884; "The Lixiviation of Silver Ores with Hyposulphite Solutions, with Special Reference to the Russell Process," New York, 1888; 2d ed., 1893. DAGGERT, ELLSWORTH, The Russell Process in its Practical Application and Economic Results, *Trans. A.I.M.E.*, Vol. 16, pp. 362–495, 1888.

[4] MORSE, W. S., The Lixiviation of Silver Ores by the Russell Process at Aspen, Colo., *Trans. A.I.M.E.*, Vol. 25, pp. 137–146, 993–997, 1895.

The ore feed to the roasting furnace was crushed to pass a 30-mesh screen; this is common practice for hyposulphite leaching.

The chloridization of the silver in the Stetefeldt furnace was 43.5 per cent; it was a little higher in the flues and dust chambers, making the average chloridization 52.5 per cent by the direct roasting operation. The roasted ore was piled on a cooling floor and allowed to remain an average of 102 hr., during which time the chloridization of the silver increased to 79.0 per cent.

The respective lixiviants mentioned above extracted the percentages of silver given below, as calculated from the average daily assays:

	Per Cent
Wash water (brine)	14.56
"Regular" solution	44.21
"Extra" solution	27.98
Total extraction	86.75

The actual extraction during the entire period of operation, based on the silver recovered and paid for, was 94.21 per cent of the silver in the roasted ore and 85.58 per cent of the silver in the raw ore. The volatilization and dust losses were 9.16 per cent of the silver, which would be fully recovered in present-day practice.

Considerable lead was dissolved by the wash water, which was precipitated with the silver as a sulphide by means of sodium sulphide. This gave a low-grade product that was expensive to refine. It was found by W. S. Morse, manager of the Aspen plant, that this precipitate, containing lead sulphide, could be utilized as a precipitant for the silver in subsequent wash waters, according to the following reaction:

$$2AgCl + PbS = Ag_2S + PbCl_2$$

This raised the grade of the final product and reduced the refining cost.

Subsequently, lead was removed from the wash water and the "regular" solution by precipitating with sodium carbonate. Lead is preferentially precipitated in this manner before the lime and magnesia.

The silver sulphide precipitate from the hyposulphite solutions was eventually refined at the plant by dissolving in hot concentrated sulphuric acid and precipitating the silver in metallic condition on copper.

Local conditions sometimes demand a variation from standard methods. In Bolivia,[1] where the metallurgical problem involves the treatment of silver-bearing tin ores, certain modifications in chloridizing roasting have been found necessary. The chief gangue minerals of the ore are pyrite and quartz. The silver occurs in tetrahedrite, jamesonite, stibnite, cylindrite, and other complex sulphantimonial minerals, which are notoriously difficult to treat by any process other than smelting. Most of the tin is present in the form of impure cassiterite, although it is sometimes present as stannite associated with the above-named minerals.

At the present time the ore is crushed dry, given a chloridizing roast, and leached with water and hyposulphite solution or with brine to extract the gold, silver, and copper. The tailings are concentrated for tin, with or without regrinding.

The percentage of silver that can be chloridized is not directly proportional to the silver content of the ore. Tailings from any grade of ore will contain 5 to 9 oz., which cannot be extracted by any known commercial solvent, even though only a small proportion of this silver is in the form of sulphide.

The average grade of ore treated assays about 35 oz. silver per ton. The ores contain 25 to 35 per cent sulphur, most of which must be removed by preliminary

[1] Sohnlein, M. G. F., Roasting and Chloridizing of Bolivian Silver-tin Ores, *Trans. A.I.M.E.*, Vol. 4, pp. 676–698, 1920.

roasting before adding salt for chloridizing. Fuel is expensive in Bolivia, so it is necessary to utilize as much as possible the heat developed by the desulphurizing roast.

A peculiarity of this ore is the loss of over 30 per cent of the silver by volatilization and in flue dust during desulphurizing roasting in a McDougall furnace, which, added to the loss from insoluble silver, makes the loss over 40 per cent. Similar but lower losses occur in hand-rabbled reverberatory furnaces. These losses can be fully recovered by means of a Cottrell precipitator, but an analysis of this product indicates that the losses are due largely to antimony, and no satisfactory process has been developed for treating it to recover the silver.

A satisfactory furnace has been finally developed in a modified form of the Edwards-Merton straight-line furnace, which has five hearths and is divided into three compartments by means of doors or dampers to control the draft. By the time the ore reaches the fifth or last hearth, it is ready for chloridization and the damper is closed, cutting off that hearth from the rest of the furnace. The necessary amount of salt is added, and the charge is chloridized in about 15 min. The chloridized ore is discharged in another 15 min. and the process repeated. This makes the operation of the furnace intermittent to some extent, but the volatilization and dust losses are greatly reduced.

Only 3.3 per cent of salt is used for chloridizing, and no extraneous fuel is required.

The chloridization of the ore is simple and quick if salt is added at the correct stage of the roast.

Samples taken every 10 min. from the chloridizing hearth for an hour after the first 15 min. show no improvement in the chloridizing by prolonging the process.

The loss of silver during roasting is 1.5 per cent. The loss as insoluble silver is 12.2 per cent, making a total recovery of 86.3 per cent. The cost of roasting only is about $1.12 per ton.

Some mining companies in Bolivia have continued to use the Patera, or hyposulphite leaching process, as the most economical for the treatment of their ores.[1] "The lack of local lead or copper smelters, and the high freight charges to the outside, prohibit the shipment of any but high-grade ores or products. Cheap salt, in unlimited amount, is available from the various closed basins of western Bolivia. Numerous semiactive volcanoes supply sulphur. Lime is also locally obtainable. Hence the Patera process, producing high-grade silver sulphides, has continued to prove an economical treatment for many high-sulphur ores that require little fuel to roast."

Segregation Process.—A process that does not seem to have attracted the notice that it should is the segregation process for the treatment of lean oxidized copper ores or of mixed oxides or sulphides. It was described by Maurice Rey.[2] It reduces the ore with carbon in the presence of a small amount of chlorine, *i.e.*, about 10 per cent of the amount of chlorine that would be required for a complete chloridization of the ore. When subjected to this combined action of chlorine and carbon, the copper is reduced on the carbon particles and tends to collect in small shot, owing to the fact that the speed of the chloridization reaction is greater than the speed of the carbon reduction. The process is particularly adaptable to highly siliceous ores. A basic gangue reduces the efficiency of the process. Sodium chloride can be replaced by magnesium chloride, cuprous chloride, cupric chloride, and calcium chloride. Potassium chloride and barium chloride are said to produce inferior results. At the Alaska mine in Southern Rhodesia a sulphide was treated which required roasting, using ½ per cent of sodium chloride and 1½ per cent of finely ground coal. These reagents were added on the sixth hearth of the roaster, segregation occurring on the sixth and seventh hearths. The ore is protected from air during cooling. It is then crushed,

[1] FERRON, ROBERT D., Blast Roasting an Improvement Over Old Patera Process in Bolivia, *Eng. Mining Jour.-Press*, Nov. 29, 1924, p. 853.

[2] *Rev. mét.*, Vol. 33, pp. 293–302, 1936.

and the copper shot or globules are recovered by crushing and concentration. A month's run on this process gave a recovery of 86.91 per cent of the contained copper.

Miscellaneous Chloridizing Roasting Processes.—Ralph W. E. MacIvor patented the use of solutions of magnesium chloride under pressure to leach roasted nickeliferous mattes early in the century; and Adolphe Seigle extended the idea to the use of calcium, sodium, magnesium, barium, strontium, or iron chlorides, specifying that the pressure must be at least 3 kg. per sq. cm. in the autoclave (1908). C. A. Brackelsberg agglomerated complex ores by mixing with magnesium or calcium chloride, magnesium sulphate, or the like, heated them to redness either in air or steam, and then treated them with hydrochloric acid and steam at 1100 to 2200°F. Under these conditions he hoped to distill nickel or cobalt chlorides out of the mass, leaving copper and iron behind (1913).

While Ralph F. Mayer took out many patents for the use of chlorine, most of them involved the use of such quantities of sulphur or of sulphur oxides that one feels as though processes were more sulphatizing operations than chloridizing. However, 1870863 of 1932 and 1937661 were exceptions. In the first the ore was moistened and mixed with ferric chloride and heated to 250° to 550°C., while air was being introduced up to 70 per cent of the amount necessary to convert the nickel and cobalt to soluble chlorides. In the second, which is intended particularly to treat Cuban laterites, the ore is reduced at 400 to 700°C., treated with chlorine gas at 150 to 300°C., and then with oxygen to convert the $FeCl_3$ to Fe_2O_3. Nickel, cobalt, and copper are supposed to remain soluble.

E. H. Brown and S. J. Broderick reduced Cuban ore with hydrogen at 600 to 700°C., then admitted chlorine at 200° or less, which is supposed to chloridize the nickel and cobalt but not the iron. If the temperature is raised to 300°C. while the chlorine is being admitted, ferrous chloride is supposed to distill off, leaving nickel, cobalt, chromium, etc. (U.S. patent 2067874). (See also p. 547.)

CHLORIDE VOLATILIZATION PROCESSES

Pohlé-Croasdale Volatilization Process.[1]—Pohlé and Croasdale discovered, by raising the temperature of chloridizing roasting to 1050°C., that gold, silver, copper, and lead can be commercially volatilized as chlorides from their ores and the metals recovered from the fumes. By charging the ore, salt, and sulphur mixture as quickly as possible into the hot zone of the furnace, volatilization begins at about 750°C. and is completed within 30 to 60 min. The roasting atmosphere must be kept highly oxidizing. The process is continuous, and the ore is commercially devoid of value as it discharges from the furnace.

The furnace used for this process was a regular cement kiln, 100 to 125 ft. in length, fired in the usual manner.

The chemical reactions involved are the same as those given for chloridizing roasting in the preceding section. There should be a strict adherence to the proportions there stated. The ore and salt are crushed to pass a 20-mesh or 0.75-mm. screen.

The process is theoretically applicable to all ores in which the metals do not occur in native or metallic condition, regardless of the gangue constituents. Basic ores are preferable because they do not fuse or sinter at the temperature of the roast. Siliceous ores work almost as well. Neutral ores are least desirable when the acid and base gangue constituents are in such proportions as to form a fusible combination with the salt at the furnace temperature. In such cases calcium chloride may be used in place of common salt, or lime may be added to the charge in sufficient quantity to raise the fusion point.

[1] CROASDALE, STUART, Volatilization of Metals as Chlorides, *Eng. Mining Jour.*, Aug. 29, 1903, pp. 312–314; U. S. patent 741712, Oct. 20, 1903.

Common salt is the usual source of chlorine on account of its cheapness, but in some instances it has been found desirable to use calcium chloride wholly or in combination with the salt. Sulphur is usually a necessary constituent of the charge, although with some ores the silica or carbonic acid seems to take its place in the chemical reactions.

Gold is easily volatilized, but in what form was never definitely determined. It was generally supposed that gold trichloride was formed at low temperatures, and this was decomposed into metallic gold and chlorine at temperatures below 300°C. If this is true, the metallic gold formed from the vapors is probably colloidal and is carried out of the furnace in that form with the gases. Rose[1] states that when gold is heated in chlorine at atmospheric pressure trichloride of gold is formed, which volatilizes at all temperatures above 180°C. up to and beyond 1100°C. Other metallurgists[2] thought that gold forms a double chloride with salt, or other metallic chlorides, and volatilizes in that form. The theory of a double chloride seems more probable.

Silver is less easily chloridized and volatilized than any of the common metals. It seems to be extremely sensitive to atmospheric conditions in the furnace and may be affected by the gangue constituents in the ore.[3] Silver chloride melts to a thin liquid at about 451°C.[4] before it volatilizes, which probably accounts for its sluggish volatilization. It is much more easily volatilized in the presence of other metallic chlorides, which would indicate that it volatilizes as a double chloride.

Lead is the most easily volatilized of all the metals as a chloride, and the chloride is easily formed by chloridizing roasting. With some ores, sulphur is not necessary in the chloridizing of lead minerals, and some experiments[5] have shown that volatilization can be accomplished more successfully without it.

Copper is readily volatilized as cupric chloride and as cuprous chloride. Cuprous chloride is the more stable at high temperatures. Some oxychlorides may be formed, but not to any large extent.

Zinc is volatilized according to the sulphur content of the ore. In oxidized ores, lead, silver, copper, and gold can be volatilized preferentially, leaving the zinc in the gangue for subsequent treatment. If complex sulphide ores are roasted so that the sulphur content is only sufficient to combine with the other base metals, these metals can, in a similar manner, be preferentially separated from the zinc by the volatilization roast, but if any excess of sulphur over the amount specified is left in the ore after the preliminary roast, zinc will volatilize with the other metals in proportion to the excess of sulphur present in the charge.

Little information is available concerning the chloridizing action on the gangue materials. Silica acts as an acid and decomposes salt, with the liberation of chlorine at high temperatures. Iron chlorides are formed from the sulphides, but they quickly decompose to the oxide, and very little of the iron is volatilized.[6] Aluminum is not volatilized as a chloride from its oxide in an oxidizing atmosphere (see page 555). Calcium and magnesium may be volatilized to some extent as chlorides,[7] but they in no way interfere with the volatilization and recovery of the other metals.

[1] Rose, Sir T. K., "Metallurgy of Gold," pp. 61–63, London, 1915

[2] Stetefeldt, *op. cit.*, p. 340.

[3] *U. S. Bur. Mines Bull.* 211, p. 45.

[4] Varley, Thomas, Superintendent, Utah Station, U. S. Bureau of Mines, Salt Lake City.

[5] Ralston, O. C., Salt in the Metallurgy of Lead, *Trans. A.I.M.E.*, Vol. 57, pp. 639–641, 1917; Varley, Thomas, *U. S. Bur. Mines Bull.* 211, footnote p. 19.

[6] Nickel volatilizes as a chloride to a greater extent than iron, and it might be possible to recover nickel in this manner. If oxidized by a preliminary roast, nickel will remain in the gangue and it is possible preferentially to volatilize copper from nickel by the chloridizing roast.

[7] Morse, W. S., Lixiviation of Silver Ores by the Russell Process at Aspen, Colo., *Trans. A.I.M.E.*, Vol. 25, p. 997, 1895.

The metallic chlorides are driven from the ore in the form of vapor, and they condense as colloidal particles of fume. Each particle is surrounded with an adsorbed film of air or furnace gas, which prevents coagulation and collection by any other means than electrical precipitation.[1] The fume particles thus enveloped will pass untouched through water or any form of scrubbing device. The electrical stresses set up in the Cottrell precipitator break up these gas envelopes and permit the coagulation and recovery of the fumes. Bag filters of textile material will make a high recovery, but are difficult and expensive to operate, owing to the corrosive nature of the fumes and gases.

The metals are recovered from the precipitated fume by the substitution of one metal for another in an aqueous solution or by the electrolysis of the fused chlorides. Where the metals in the fume consist only of copper, silver, and gold, or lead, silver, and gold, the fumes are reduced to a bullion by heating with lime and carbon. The calcium-chloride slag can be utilized in place of salt to chloridize new ore.

Several small plants have been operated in the United States, but they were equipped with furnaces ranging from 25 to 60 ft. in length. These furnaces were too short to complete the volatilization when operating at commercial capacity. A full-sized plant was operated by the Blaisdell Coscotitlan Syndicate,[2] Pachuca, Hidalgo, Mexico, on patio tailings. Their furnace was a kiln 125 ft. long and 8 ft. in diameter, lined with 9-in. concrete clinker brick. The fuel consumption was 12 gal. of 18,500 B.t.u. oil per dry metric ton and this without preheating the air or ore, or using any insulation. The recoveries were well over 90 per cent on the gold, copper, and mercury; 100 per cent on the small amount of lead; and 75 per cent on the silver, which was considered good on this class of material. No advantage was found by using calcium chloride, but 5 per cent of lime was necessary to reach the proper finishing temperature. The property was forced to cease operations on account of the low price of silver.

A commercial plant was put into operation on the same line by the Western Metallurgical Co. of Los Angeles in 1927. It was found advantageous to add the salt at successive intervals during the roast, rather than all at once with the ore. By doing so the fusing temperature of the charge was maintained at a higher point, and the chloridization, consequently the volatilization of the metals, considerably increased. The ore was preheated to the volatilization temperature in a separate furnace before adding the salt. The salt and the hot ore were then fed into another furnace, maintained at the volatilization temperature with a comparatively small amount of fuel, and the chloride fumes sent to the Cottrell treaters less contaminated with combustion gases and other inert material. Certain advantages were also found in passing the ore charge through the furnace concurrently with the combustion gases, instead of countercurrently as originally practiced, but this system was not developed commercially. The plant fell a victim to the Great Depression.

Maier[3] has discovered that lead and zinc are readily and almost completely volatilized as chlorides when their oxides (in ores) are heated, without reducing agents, in a current of chlorine gas at temperatures ranging from 500 to 750°C. The chlorides of both metals are volatilized and easily condensed in a relatively pure condition; the principal impurity is calcium chloride—and magnesium chloride would probably volatilize also if present in the ore. Iron and aluminum chlorides are decomposed at low temperatures and do not volatilize to any appreciable extent.

[1] BANCROFT, W. D., "Applied Colloidal Chemistry," pp. 21–22, 291–300, New York and London, 1921.

[2] *U. S. Bur. Mines Bull.* 211, pp. 83–84.

[3] MAIER, CHARLES G., Possibilities of Dry Chlorination of Oxidized Zinc Materials, *Eng. Min. Jour.-Press* (January 13, 1923), p. 51.

This research work has been carefully done and is suggestive of further application of the process.

Chlorine volatilization processes have been patented by Wescott (U.S. patents 1552786, 1898702, and 1916853) and by Hart [1826932 (reissue 18609), 2030867, and 2030868] for the beneficiation of iron ores containing such metals as nickel, chromium, cobalt, and copper. The iron was to be volatilized as $FeCl_3$, which was burned to pure Fe_2O_3 and Cl (the former being used as an iron ore, the latter used again in the process), leaving a residue behind containing the more valuable metals as chlorides, mixed with the gangue. Hart also contemplated treating such ores as the Cuban North Coast ores, volatilizing only a part of the iron, leaving a residue to be smelted to 18 and 8 stainless steel. It is believed by the editor that he did not realize how much chlorine remains as basic chlorides or nickel chloride under a partial volatilization program. The Wescott process for selective chloridization of nickel is described in the chapter on nickel.

Alexander L. D. Adrian, along somewhat the same lines as Wescott and Hart, had previously patented a process that involved briquetting finely ground complex ores with sawdust and molasses, or starch and water, carbonizing in a muffle, and then introducing chlorine gas at a temperature above 450°C. Iron was supposed to distill off as ferric chloride, leaving behind such metals as chromium, zirconium, vanadium, uranium, cobalt, and nickel (U.S. patent 1434485 of 1922).

Caveat Process of Tin Recovery.—This process was worked out for the treatment of the ores of Pinyok, Thailand. These ores contain tin as cassiterite in a gangue containing considerable magnetite and iron-lime garnet. The grain size of the cassiterite was so small and the interfering minerals of such magnitude that both gravity concentration and flotation gave indifferent results for the recovery of tin. A large number of chemical processes were experimented with and the so-called Caveat process was eventually decided upon as offering the best chance of working these ores profitably.

Essentially the process was the treatment of a mixture of the ore and ferrous or calcium chloride under reducing conditions such that none of the iron was left as Fe_2O_3 and a large part of it was reduced to FeO or Fe. Under these conditions the stannic oxide was reduced to stannous oxide, and in this form it reacted with the chlorine present to give stannous chloride and ferrous oxide or calcium oxide, depending on which chloride was used. As a matter of scientific interest it may be noted that the reaction was satisfactory with barium or strontium chloride, but these were of course out of the question because of price. Sodium and potassium chlorides gave poor results.

The optimum working temperature lay between 725 and 750°C. At too low a temperature, the retorts were corroded and the reaction was of course slow; at too high a temperature, the reaction again became slow and there was grave risk of burning out the retorts. A most ingenious furnace for continuous retorting was invented by A. G. MacGregor of London.

The volatilized stannous chloride was condensed in water, this problem being comparatively easy as the products of combustion of the fuel used in heating the furnace were kept separate from the volatilized chloride, which was mixed only with carbon monoxide or carbon dioxide from the reduction and a negligible amount of air trapped by the ore, the reduction carbon, and the chloride.

The scrubber solution was reduced and practically neutralized with scrap iron and then electrolyzed, using a revolving steel mandrel as the cathode and boiler-plate or cast-iron anodes. The tin was deposited on the rotating mandrel and was replaced in the solution by an equivalent amount of the iron of the anode. The Pinyok ore contains some lead, which was also volatilized as chloride. While most of the lead

deposited as a sludge in the acid scrubber solution, the solution as sent to the tank house was always saturated with lead chloride to the extent permitted by the temperature and the slight acidity of the solution. Practically all the tin could be deposited before the lead began to plate out.

The solutions were stripped of tin after the main portion of tin had been taken off the cathode, the lead coming down with this last tin and producing a small amount of inferior metal.

The tank-house solutions were evaporated, recovering ferrous chloride derived from the metal of the anode, and this chloride then went back into the process with more ore and reducing agent (charcoal). As a consequence, after operations were initiated, except if calcium chloride was used for make-up, the reactive reagent was ferrous chloride. A pilot plant was operated at Bromley-le-Bow near London. The full-scale plant was just ready to run at the time of the Japanese invasion of Thailand, and the plant was taken over by them in the first few days.

In very recent months Irving E. Muskat has taken out patents for the volatilization of stannic chloride from tin ores and residues in a continuous shaft furnace. He has a tin-ore treatment process in which he chloridizes tin ores at such a rate as to make the reaction self-sustaining, using chlorine or hydrochloric acid in a refractory-lined shaft furnace (U.S. patent 2345210 of Mar. 28, 1944). Some reducing agent is necessary, such as carbon, methane, acetylene, ethane, sulphur, or a sulphide. In spite of the necessity for a reducing agent, he also finds it occasionally necessary to introduce air or oxygen, in which case the reducing agent must be increased. The presence of air renders selective chlorination possible, particularly as it inhibits the formation of iron chlorides.

Other uses of the chlorine radical in the tin metallurgy are of course old. The late J. W. Richards for some time ran a plant for detinning the ordinary tin plate, using hydrochloric acid as the detinning agent and producing a tin chloride that was sold. This plant was eventually forced out of business by the rise of the electrolytic detinning process using a caustic soda electrolyte. In turn the use of chlorine for detinning came back in the Goldschmidt process where steel scrap was detinned by gaseous chlorine (page 554).

Continuous Chromite Chloridization.—It is claimed that it is possible to chloridize chromite continuously, distilling off the chromium from the iron (Irving E. Muskat, U. S. patent 2325192 of July 27, 1943). A reducing agent is mixed with the ore in a refractory-lined container, using chlorine not in excess of the theoretical amount to chloridize the chromium and the iron to the "ic" condition. The chromium chloride distills off and is condensed after adding an excess of chlorine to the gas being drawn off from the reactor.

The use of sulphur dichloride, SCl_2, as a chloridizing agent, with sulphur tetrachloride, SCl_4, as a welcome impurity, has been advocated by L. G. Jenness (U.S. patents 1834622 of 1931; 1863999 of 1932; 1923094 of 1933), particularly in combination with free chlorine. The so-called monochloride (S_2Cl_2) he finds inert, which bears out the earlier experience of Dr. E. W. Wescott, who used SCl_2 (or S_2Cl_4, as it more probably is) to chloridize pyrrhotite for the production of ferric chloride and elemental sulphur. This latter process, however, lies out of the field of nonferrous metallurgy.

Sulphur dichloride is prepared by passing chlorine through or over sulphur or sulphur chloride at 25 to 60°C. Above 60°C. the product is contaminated with sulphur monochloride, this undesirable feature increasing as the temperate approaches 100°C. Jenness conducts his operations by working at increasing temperatures, thereby volatilizing one chloride after another. He believes that when he works on oxidized ores, much of the volatilized product consists of double chlorides, *e.g.*, $4TaCl_5.3SCl_2$, $TiCl_4.SCl_2$, $2CbCl_5.SCl_2$, $VOCl_3.SCl_2$, and that such chlorides are

distinctly lower in their volatilizing points than are the corresponding chlorides, such as $TaCl_5$, $CbCl_5$, etc. The double chlorides he also says are most of them soluble without change in water, while the single chlorides hydrolyze. The double chloride of tin is an exception, as it rapidly decomposes even in cold water.

Oxide Volatilization.—Corollary to chloride volatilization is the oxide volatilization process, developed by the Chief Consolidated Mining Co.,[1] at Eureka, Utah. Ores from this mine vary from entirely oxidized ores to ores showing only slight oxidization, and from nearly self-fluxing ores to highly infusible ores. The average ore has approximately the following composition: Au, 0.055 oz. per ton; Ag, 25.2 oz. per ton; Pb, 6.0; Zn, 4.6; Fe, 7.0; "insoluble," 63.8; S, 4.8; and CaO, 2.6 per cent. Smelting and freight charges were high, so the company began its metallurgical research in 1916 to develop a method of ore treatment at the mine, principally along the lines of mechanical concentration and chloride volatilization. This work resulted in the construction of a concentration and volatilization plant, designed to treat 250 tons of ore per day; the plant was started in May, 1925, but was scrapped in 1932, due to low metal prices.

All the sulphide minerals and some of the lead carbonate are recovered by gravity concentration and flotation; this likewise removes all the easily fusible or slag-forming constituents from the gangue. The tailings from the concentrating plant carry 0.035 oz. Au per ton; 11.4 oz. Ag per ton; and 4.7 per cent Pb. These tailings are filtered and then dried by the hot gases from the volatilization furnace in a Ruggles-Coles rotary drier, 7.5 ft. in diameter and 60 ft. long. An indirect-heat type of drier is used to avoid contamination of the fume-bearing gas.

The dried tailings go direct to the volatilization furnace, which is the regular cement kiln type, 10 ft. in diameter and 80 ft. long, and is fired with pulverized coal. Volatilization experiments were started by using 10 per cent salt, but this produced a fusible slag at temperatures below the point at which a satisfactory volatilization of the silver could be obtained. Reduction of the percentage of salt permitted the raising of roasting temperatures which thereby increased the volatilization and recovery of the silver, until, finally, the use of salt or other chlorides was discontinued entirely and the furnace temperature was raised to 1400°C., at which point the gold, silver, and lead are almost completely volatilized. These results have been duplicated in practice, and the elimination of chlorine permits the use of bags for the recovery of the volatilized fume. The calcines discharging from the volatilizing furnace carry only trace Au; 1.2 oz. Ag per ton; and 0.2 per cent Pb, thereby showing a recovery of nearly 100 per cent of the gold, 90 per cent of the silver, and over 95 per cent of the lead, since the recovery of fume by means of the baghouse is practically complete. The recovered fume assays 0.3 oz. Au per ton; 64.0 oz. Ag per ton; and 27.8 per cent Pb. The capacity of this furnace is 7 tons of tailings per hour, and the consumption of coal is about 30 per cent of the furnace feed. The tailings go to the volatilizing furnace without regrinding and will all pass a 20-mesh or 0.75-mm. screen.

Two curious analogies have developed between chloride and oxide volatilization: (1) Accretions of ore occur in the preheating zone of the volatilizing furnace, up to a temperature of about 1100°C., in spite of the fact that no salt or other chlorides are used in the ore feed, but at higher temperatures these accretions do not exist. They are not slagged accretions, such as rings in cement kilns, but consist of unfused particles of quartz (the principal gangue), loosely bound together by a slight fusion of the other gangue constituents; they do not occur in definite rings, as in cement kilns, but

[1] PARSONS, ARTHUR B., Chief Consolidated Starts Novel Reduction Plant, *Eng. Min. Jour.-Press* (Oct. 11, 1924), p. 582; BARBOUR, PERCY E., The New Utah-Idaho Metallurgy, *Min Met.* (August, 1925), p. 365; WIGTON, G. H., The Chief Consolidated Volatilization Process and Mill, *Trans. A.I.M.E.* (September, 1925); *Min. Met.* (August, 1925), p. 444.

occupy the entire preheating zone. These accretions are removed periodically by means of a water-cooled plow mounted on the end of a water-cooled bar, 86 ft. long, which has a direct-current crane motor and gears mounted on the other end; the gears run on a stationary steel rack mounted on each side of the bar. With this plow, longitudinal trenches can be cut through the accretions when necessary and a clean furnace maintained. The actual plowing operation requires about 20 min. (2) As ordinarily operated, i.e., passing the feed countercurrently with the furnace gases, considerable trouble was experienced with the large amount of flue dust that passed over with the fume and required re-treatment. The ore now is passed concurrently with the gases and, consequently, is fed at once into the hottest part of the furnace; the quick heating softens the ore so that there is almost no dusting. The volatilization is about the same, and the fume carries only about 15 per cent silica. The accretions occur, also, near the end of the furnace, where they can be removed more easily. The advantage of getting the ore feed quickly into the hottest zone of the furnace was observed by Croasdale and by all subsequent investigators of chloride volatilization. The Western Metallurgical Co. observed certain advantages in passing the ore feed concurrently with the gases (see preceding section on chloride volatilization).

The Waelz process is an outstanding oxide volatilization process, but this is treated at length in the chapter on zinc. The methods of making zinc oxide and leaded zinc oxide are also oxide-volatilization processes. The Schwarz oxide-volatilization process demands some notice. Alfred Schwarz discovered that if a sulphide ore were ground to about 20 mesh with about 50 per cent of powdered coal, and the product mixed with about ⅔ per cent of its weight of starch, glue, or other similar binder in a 1 per cent solution, together with about half the weight of the weight of the ore in fine cinder from previous runs, the mix ignited readily on a perforated grate and was porous enough to burn readily, with almost complete volatilization of zinc, lead, and silver. If the ore was a pure blende, the product (zinc oxide) was of fair color, but required roasting to free it from mechanically held sulphur dioxide. Before the great improvements in flotation, the author felt the process had a field as a pyro-concentration process, giving an almost pure lead-zinc-silver oxide product (arsenic and antimony of course were with the volatilized portion) and a residue containing copper and gold. C. A. H. de Saulles about the same time that Schwarz was working (1921) patented a process for feeding a mixture of ore and reducing agent on to a bath of molten slag, the zinc and lead reducing, volatilizing, and then reoxidizing above the charge, while all nonvolatile constituents went into the slag (U.S. patent 1712553).

A plant is understood to be under construction in Bolivia (1943) from designs by U. C. Tainton, in which tin ores are to be burned with carbon and pyrite on a grate, the tin being lirst sulphidized and volatilized, then burned above the charge to SnO_2 and SO_2, the tin oxide being swept out and collected. The thought is to effect a pyro-concentration of the tin.

Volatilization Processes for the Production of Aluminum Chloride and Aluminum. Aluminum was first commercially produced by the Deville process or its modifications. The process consisted of heating alumina and carbon in a retort in an atmosphere of chlorine gas. Aluminum chloride volatilized and was recovered by condensation. In later practice, salt was added to the retort and the double chloride of sodium and aluminum was formed and recovered in the same manner. Metallic aluminum was produced by reduction of this salt with metallic sodium. This process was abandoned a number of years ago as a source of aluminum, but anhydrous aluminum chloride has assumed considerable importance in the petroleum industry.

Since most of the methods for producing aluminum chloride involve the use of chlorine gas in conjunction with volatilization, the subject will be discussed more

fully under Dry Chlorine-gas Processes (next page). There are, however, several methods proposed which are strictly volatilization processes. One is that of Booth and Marshall,[1] in which aluminum silicate (clay or feldspar) or aluminum sulphate (alunite) is mixed with calcium or magnesium chloride and heated in an electric furnace to a temperature of 1300°C. An alkaline-earth silicate is formed, and aluminum chloride is recovered by volatilization and condensation.

Another method is proposed by Burgess.[2] He mixes aluminum carbide with an anhydrous chloride of an element below aluminum in the electrochemical series and ignites the mixture. The reaction begins at 380°C. and is exothermic. The aluminum chloride volatilizes and is recovered by condensation. Lead chloride and silicon tetrachloride are suggested as the cheapest chloridizing agents for the aluminum carbide.

Ravner and Goldschmidt[3] propose using minerals of the feldspar group as a source of alumina, because they contain 25 to 36 per cent alumina and very little iron. When mixed with carbon they will react to form aluminum chloride in the same manner that pure alumina and carbon react, and at the same temperatures.

Wolcott[4] proposes using oil shale, bituminous shale, and bone coal as raw materials for the production of aluminum chloride since the reducing agent and the aluminiferous material are already most intimately blended and ready to react. The only difficulty is that the alumina and the carbon seldom exist in the proper proportions, but, with low-grade coals, the excess of carbon is utilized as fuel for the process. This material is roasted with salt, and the aluminum chloride is volatilized and recovered as fume.

WET CHLORINE-GAS PROCESSES

The Plattner process was in constant use, since it was first proposed by Plattner in 1851, until about 1916. It is applicable only for the recovery of gold, and for a long time it was used principally for the treatment of concentrates from free-milling ores. The operations were, therefore, conducted on a small scale. The pyritic concentrates were roasted "dead" in a hand reverberatory furnace and then placed in a vat and leached with water saturated with chlorine gas. Owing to the difficulty in handling chlorine gas in this manner, the vat was replaced by a lead-lined iron barrel having a capacity of about 1 ton of ore. Water, bleaching powder, and sulphuric acid were added to the ore in the barrel in such proportions as to form a thin pulp and to generate a slight gas pressure when the barrel was sealed and the charge agitated. The chlorination of the gold was completed after the barrel had been revolved for a few hours. The charge was then dumped into an open vat provided with a sand filter, and washed with water. The gold was precipitated by ferrous sulphate, collected, and melted into bullion.

In 1894 the process was first applied to crude ores from Cripple Creek, Colo. There was no change in the process except to conduct it on a larger scale. The ore was crushed to pass a 12-mesh or 1.5-mm. screen and roasted in a mechanical furnace. The lead-lined chlorination barrels were enlarged to 10 tons capacity and were provided with perforated lead filters inside. The chlorination was done under pressure with bleaching powder and acid as before; 12 lb. of bleaching powder and 24 lb. of acid were required per ton of ore. The barrels were revolved 2 or 3 hr. and then stopped with the filter at the bottom. A valve was opened under the filter, and the leaching and washing were done in the barrel. The tailings were discharged directly

[1] U. S. patents 1392043 to 1392046, Sept. 27, 1921, H. S. Booth and G. G. Marshall.
[2] U. S. patent 1321281, Louis Burgess, Nov. 11, 1919.
[3] U. S. patent 1302852, May 6, 1919, Ostein Ravner and Victor M. Goldschmidt.
[4] English patent 160759; Canadian patent 217051; U. S. patent pending, E. R. Wolcott.

from the barrel to the dump. In some instances the gold was precipitated from solution by filtering through charcoal. After a certain time the charcoal was burned and the gold-bearing ashes melted into bullion. Generally, the gold was precipitated by means of sulphureted hydrogen and melted into bullion by fluxing this precipitate. In later practice on Cripple Creek ores, the chlorine was generated by the electrolysis of salt and was absorbed by water as it passed through scrubbing towers 30 in. in diameter and 30 ft. high, made of ordinary glazed sewer pipe. From the towers the saturated solution of gas was pumped into lead-lined storage tanks and then run into the chlorination barrels as needed. The agitation of the charge produced sufficient gas pressure. The rest of the process remained the same as before.

The treatment of Cripple Creek ores by this process continued until 1911, when it was finally supplanted by the cyanide process. During its operation 2,046,223 tons of ore were treated at an average cost of $2.34 per ton. The tailings averaged 0.063 oz. per ton, and the average recovery of gold was 93.23 per cent.

A few chlorination plants continued to treat pyritic concentrates in California up to the time of the First World War, but this marked the close of the chlorination process in the United States and it is doubtful if it will ever be revived. It is not adapted to ores containing any free basic gangue, owing to the excessive consumption of chlorine. It has been replaced generally by the cheaper and more adaptable cyanide process.

Vanadium Ores.—Early in 1924, Dr. Saklatwalla, while research chemist for the Vanadium Corp. of America, developed a process for the extraction of vanadium and some of the rarer metals from vanadium ores by the use of chlorine gas in cold solution, but the ores that are being treated today are too low grade for this purpose.

DRY CHLORINE-GAS PROCESSES

Chlorine Production.—With the development of electrolytic processes for the production of caustic soda and chlorine from salt, and with modern methods for drying, liquefying, and transporting chlorine in a liquid state, this element has become a cheap commodity available for many uses and capable of considerable development metallurgically. The actual continuous working capacity for chlorine production in the United States at the present time is about 2800 tons per day, which does not include the chlorine made and used in the same plant.

Malm Process for Complex Ores.[1]—This process was a development of the Baker-Burwell process, described on page 522, for low-grade complex sulphide ores. The ore was crushed on the average to pass a 0.75-mm. screen. The dry ore was fed into a tube mill countercurrently with a stream of dry chlorine gas. The tube mill was divided into three compartments and was not lined. No grinding was done in the tube mill, but a few pebbles were added to keep the charge from forming into lumps. Most of the chlorination was done in the compartment at the discharge end where the chlorine gas entered. The central compartment was arranged so as to be heated on the outside of the shell if necessary to start chemical action or to keep chemical action alive if the ore contains little sulphur. The temperature in the the tube mill was kept near 70°C., which was still lower than that used in the Baker-Burwell process. About 50 per cent of the chlorination was done in the tube mill, or enough chlorine was admitted here to chloridize all the recoverable metals. If complete chlorination was attempted in the tube mill, the temperature of the charge had to be raised above the melting point of the free sulphur present and the charge became sticky.

The chemical reactions may be simply expressed by the equation

$$XS + Cl_2 = XCl_2 + S$$

[1] IONIDES, S. A., The Dry Chlorination of Complex Ores, *Mining Sci. Press*, May 27, 1916, pp. 781–787.

Very little sulphur chloride was formed, and if the charge was kept free from moisture no hydrochloric acid was formed. The ore discharged from the tube mill into a multiple-hearth furnace, where the temperature was raised by direct firing but was not allowed to go higher than 400°C. This decomposed the iron chlorides and converted most of the iron into the oxide. The chlorine liberated was absorbed by fresh sulphide ore, which was continually circulated on the two upper hearths of the furnace. The tube-mill discharge was delivered only on the four lower hearths where the chlorination was completed.

From the furnace, the chloridized ore was discharged into an agitator filter, where it was first washed with mill solution which contained the soluble metallic chlorides from previous charges. These were principally chlorides of iron, zinc, and copper. This mill solution dissolved all the metallic chlorides, except the lead chloride and sulphate. The mill solution was followed by a wash of steam, which cleaned the charge of soluble metallic chlorides with a minimum amount of water. The wash waters went to storage to build up new mill solution. The ore was then leached with a hot saturated solution of common salt which dissolved the lead salts. This solution was conveyed to a separate tank, where it was allowed to cool and the lead chloride crystallized out. The lead chloride was collected, fused, and electrolyzed for the recovery of lead and chlorine. The anodes were graphite and the cathodes molten lead, which was tapped periodically from the cell. The chlorine was returned to the circuit.

When the mill solution became saturated with soluble metallic chlorides, it was treated with metallic lead to precipitate the gold, silver, and copper; then with zinc to precipitate any lead that may have gone into solution; and then with zinc oxide (obtained by roasting high-grade ore) to precipitate all the iron, manganese, and other impurities. This left a commercially pure solution of zinc chloride. The precipitate was filtered off and the zinc chloride solution evaporated to a 70 per cent solution if the product desired was zinc chloride; and to dryness, if the process was carried on to the production of metallic zinc and the recovery of the chlorine. (If the product is sold as zinc chloride, the new chlorine supply must be generated by the electrolysis of salt solution. If the final product is metallic zinc, the anhydrous chloride is fused and electrolyzed by using molten zinc as a cathode and graphite as an anode.) The zinc was tapped periodically and the chlorine returned to the circuit. The cells for the electrolysis of both lead and zinc were of the same pattern. They were made of concrete and lined with a special fire-clay tile. They gave entire satisfaction under continuous operation. The evaporation of the zinc chloride solution, which has always been troublesome not only from its corrosive qualities but from its tendency to form basic salts, was conducted in a specially designed pan without difficulty from either of these sources.

The recovery of all metals by this process was said to average between 90 and 95 per cent. A pilot plant was constructed in Denver during 1924–1925 for the production of zinc chloride by this process. It is reported that this plant was operated continuously for several months with satisfactory metallurgical results, but no market could be found in that territory for the zinc chloride and the caustic soda produced; also, some difficulty was experienced in using the wet chlorine gas direct from the electrolytic cells.

A plant using chlorine gas for the treatment of lead-zinc ores is reported to have been in commercial operation at Weston Point, England, in 1924[1] and for some years thereafter.

[1] Potter, J. G., Complex Lead-Zinc Ores to Be Treated by Chlorination and Electrolysis, *Eng. Min. Jour.-Press*, Apr. 19, 1924, p. 646.

Detinning Processes.—These may be summed up in the Goldschmidt process,[1] although there are several modifications and patents that are closely related. They are all based on the fact that dry chlorine gas will attack tin, but will not attack iron to any appreciable extent. Therefore, if dry chlorine gas is carried over and through tin scrap, the chlorine and the tin combine, with the evolution of considerable heat, forming tin tetrachloride, which is a heavy fuming liquid and drops off the scrap. The tin scrap must be absolutely dry and free from all organic substances, paper, lacquer, etc. It is not only necessary to remove all moisture, but also all substances that can produce or attract moisture in order to prevent corrosion of the iron which would make it unmarketable. The tin scrap is compressed into bundles and placed into cylinders which are then closed. Chlorine gas is introduced at a pressure of several atmospheres. As the tin chloride is formed, the pressure drops. As soon as the pressure remains constant, the detinning is complete. Artificial cooling must be provided to prevent overheating.

The chlorine and the tin chloride are removed and the iron scrap bundles are carefully washed and sold to open-hearth steel works. The tin tetrachloride was formerly sold to the silk mills for weighting silk. In a modification[2] of this process the chlorine gas is dissolved in carbon tetrachloride and the tin scrap is placed in this solution, which dissolves the tin tetrachloride as rapidly as it is formed and is thus withdrawn from the scrap. In another process[3] the scrap is heated with sand until the tin becomes brittle at temperature near the melting point. The mixture is then tumbled in a barrel until the tin is completely removed from the iron. The sand and the tin are screened from the scrap and are treated with dry chlorine gas in a closed vessel at a temperature that will volatilize and distill off the stannic chloride. A small plant near London used this process for a time.

Miscellaneous Processes.—The use of chlorine to form aluminum chloride is noted below at length. In the chapter on magnesium, the large-scale formation of magnesium chloride has been described. The use of fused chloride baths for the production of barium, strontium, calcium, and lithium is an important factor in their metallurgy. Beryllium chloride has been used for the production of beryllium, but the fluoride seems to be more favored.

Aluminum Chloride Processes.—Anhydrous aluminum chloride possesses remarkable properties as a catalyst or reagent for the treatment of petroleum according to the Friedel & Crafts reaction: (1) It converts all unsaturated compounds into saturated compounds by throwing out the excess of carbon in the unsaturated hydrocarbons. In this manner it converts unstable oils from asphalt-base petroleums into stable products of good odor and color similar to the paraffin-base petroleums. (2) By simply boiling the heavier petroleum oils with anhydrous aluminum chloride at atmospheric pressure, these oils are cracked and 60 to 85 per cent of the heavy oil is converted into low-boiling fractions, leaving a residue of coke, or, if the distillation is stopped at the proper time, 60 per cent of the low-boiling fractions is produced, leaving 20 to 25 per cent of good lubricating stock. (3) It completely desulphurizes the petroleum during refining.

The value of this reagent in the petroleum industry is so pronounced that over 700 patents have already been issued covering processes for its production, and practically all the oil companies at one time or another have been engaged in research work relative to its commercial application.

[1] GOLDSCHMIDT, KARL, The Detinning Industry, *Electrochem. Met. Ind.* (now *Chem. Met. Eng.*), Vol. 7, pp. 79–81, Feb., 1909.

[2] U. S. patent 943986, MURRAY and FERNBERGER, 1909.

[3] U. S. patent 958877, C. J. REED, 1910.

Aluminum chloride is a white crystalline solid which volatilizes without fusing between 181 and 195°C. It is extremely hygroscopic and absorbs moisture from the air to form aluminum oxide and hydrochloric acid. This easy decomposition seriously interferes with its action as a catalyzer; it also produces transportation and storage problems on account of the difficulty of securing suitable moisture-proof containers.

The methods proposed for the manufacture of anhydrous aluminum chloride may be grouped under the following headings (reference to the technical paper quoted or to the original patents must be made for the details of these processes): (1) dry chlorine gas acting on aluminum metal; (2) dry hydrochloric acid gas acting on aluminum metal; (3) chlorine gas acting on mixtures of aluminiferous and carbonaceous materials; (4) chlorine gas or hydrogen chloride acting on aluminum carbide; (5) chlorine gas acting on aluminum nitride; (6) chlorine gas and carbon disulphide vapor acting on aluminiferous materials; (7) chlorine compounds of carbon acting on aluminiferous materials; (8) chlorine compounds of sulphur or arsenic acting on aluminiferous materials; (9) dry lead chloride reacting with aluminum metal or with aluminum carbide; (10) anhydrous calcium chloride reacting with aluminiferous materials; (11) aluminum chloride solutions prepared by any wet method, then evaporated and the crystals dehydrated.

The use of chlorine in refining metallic gold is described in the chapter on gold and silver refining. A stream of chlorine bubbled through molten aluminum is used in the aluminum-casting industry to keep the metal pure and to afford a protection against oxygen.

Nickel and Cobalt Ore.—Chlorine has been successfully applied in the laboratory to the recovery of nickel and cobalt from arsenical ores.[1] The Diehl process for treatment of nickel ores containing large amounts of magnesia and lime is interesting chemically, and suggestive of how basic ores may be leached. The ore, moistened with hydrochloric acid, is tube-milled at about 500°F. in an atmosphere of hydrochloric acid gas and then sent to a leaching tank with water. This water will take out practically nothing but a calcium-magnesium chloride solution, which is evaporated and treated with sulphuric acid to regenerate hydrochloric acid gas or is evaporated to hydrolyze the chlorides. The ore after leaching with water is leached again with hydrochloric acid, which then dissolves the nickel.

Cuban ore treatment with hydrochloric acid for the recovery of nickel and cobalt was devised by W. G. Hubler and F. R. Archibald. The ore is leached with hydrochloric acid (4 to 20 per cent in strength) until the free acid is less than 7 per cent. The solution is then filtered off and precipitated with magnesia. Iron and aluminum come down first, then nickel and cobalt. The magnesium chloride solution is then evaporated and the chloride hydrolyzed, thus recovering the magnesia and acid.

Electrolytic iron was produced with a chloride electrolyte for a time by the Electrolytic Iron Co. of America. The iron had the advantage of being sulphur-free. The process used scrap iron as a base, with carbon anodes, and rotating mandrels as cathodes. Pregnant ferrous chloride solution was fed into the cathode cell and ferric chloride solution withdrawn from the anode compartment, a sheet-asbestos diaphragm separating the two. This ferric chloride solution was then used as a solvent for the scrap iron. Some unascertained impurity was evidently picked up from it, for with old electrolytes the deposit would split and the revolving pieces cut the diaphragms.

[1] Brallier, *op. cit.*, p. 849.

CHAPTER XVIII

CHROMIUM

BY ENOCH PERKINS[1]

Physical Constants.[2]—According to Becket[1], differences in purity and in the elements making up the impurities in chromium have in the past resulted in discrepancies in its physical constants, but with the production of electrolytic chromium, more accurate figures have been possible. Constants for pure chromium are given by Becket as follows:

Atomic weight (accurate), 52.01.
Density, 7.1.
Melting point, probably most accurate figure, 1830°C.
Boiling point (author believes this figure too low), 2200°C.
Hardness cast chromium, Mohs' scale, 4 to 5.
Hardness cast chromium (commercial), Brinell number, 98.66% Cr, 0.02C., 130.
Hardness cast electrolytic chromium, Brinell number (different observers), 90–115.
Hardness chromium plating, Mohs' scale, 8–9.
Hardness chromium plating, Brinell number, 800–900.
Specific heat between 0 and 100°C., 0.12.
Electrical resistivity, microhms per centimeter cube, 13.
Linear coefficient of thermal expansion, room temperature, 8.2×10^{-6}.
Magnetic susceptibility, extremely feeble.
Crystal structure, body-centered cubic.

Chromite.—This mineral with a specific gravity of 4.4 and a 5.5 hardness is the source of all chromium products and is one of the most refractory substances known. The theoretical formula for chromite is $FeO.Cr_2O_3$, though it does not appear as such in nature owing to replacement of FeO with MgO or Cr_2O_3 with Al_2O_3 or Fe_2O_3. Consequently, the formula could more practically be written $(Fe,Mg)O.(Cr,Al,Fe)_2O_3$. The extent to which the various elements may replace one another in the mineral crystal is evident when comparing the theoretical and actual chromium-iron ratios for various chrome ores. A pure chromite would contain 68 per cent Cr_2O_3 and 32 FeO, resulting in a chromium-iron ratio of 1.87:1 as against the actual chromium-iron ratios in chrome ores, which vary from less than 1:1 to as much as 4:1.

Grades of Chrome Ore.—For the needs of industry, chrome ore is classified into three main categories: metallurgical, refractory, and chemical.

Metallurgical Chrome Ore.—There are two qualities of metallurgical chrome ores—those suitable for low-carbon ferrochrome and those suitable for high-carbon ferrochrome manufacture. The manufacturers of high-carbon ferrochrome prefer an ore running 48 per cent Cr_2O_3 or better, with a chromium-iron ratio of at least 3:1. Silica is undesirable, and some producers are reluctant to use an ore whose combined magnesia and alumina content is in excess of 25 per cent. The ore should be lumpy,

[1] Vice-president, Mutual Chemical Co. of America, New York.
[2] References in this chapter are to similarly numbered references in the Bibliography at the close of the chapter.

with not more than 15 per cent going through a ½-in. screen. Massive ore resistant to attrition is very desirable.

Chrome ore fines or concentrates may be used as part of the raw material in the manufacture of low-carbon ferrochrome, but if the material consists of screenings it is often washed in order to remove tramp wood, since carbon is undesirable in this process. Likewise, acid-washed chrome ore with a high carbon content is disadvantageous in certain processes. The ore should run at least 48 per cent Cr_2O_3 with a chromium-iron ratio preferably in excess of 3:1.

Refractory Ore.—The physical make-up of chrome ore for refractory use is of great importance. A hard massive ore is preferred, and concentrates are less desirable for some refractory purposes than fines secured from grinding lump. The ore should be uniform in Cr_2O_3 content, particularly when used as lump in the maintenance of open-hearth furnaces in the steel industry. A high Cr_2O_3 content is less important than in the case of metallurgical ores. High alumina and magnesia and low silica and iron contents are specified.

Standard refractory ores usually carry approximately 33 per cent Cr_2O_3, 30 per cent Al_2O_3, 17 per cent MgO, and 10 per cent iron, with the silica as low as 2 per cent.

Chemical Ore.—The determining factor in classifying chrome ores for use in the manufacture of chromium chemicals is the cost per unit of Cr_2O_3 rather than analysis or physical make-up. High-grade ores which provide some unit increase in output are consumed in the chemical industry only provided the cost per unit of Cr_2O_3 is consistent with lower grade competitive ores. While ores running 48 per cent Cr_2O_3 or better have been consumed in considerable quantities in the chemical industry, the most important chemical ore originates from the Transvaal, analyzing 44 per cent Cr_2O_3, with a chromium-iron ratio in the neighborhood of 1.6:1, 4 per cent silica, 15 per cent alumina, and 9 per cent MgO. High silica is a disadvantage, as are iron and alumina, but to a lesser degree. The ore is usually in the form of run-of-mine fines with only occasional lumps.

Chromium Metal.—Chromium metal may be produced in commercial quantities by the Goldschmidt process, electric-furnace process, or electrolytically. The Goldschmidt process is based on an aluminothermic reaction which, once under way, continues as exothermic. Chromium is added to the mix in the form of chrome-oxide green carrying in excess of 99 per cent Cr_2O_3 with not more than 0.003 sulphur. The reduction is brought about through the addition of aluminum powder, producing a chromium metal analyzing approximately as follows: Cr, 98 to 99 per cent; Fe, 0.3 to 0.5; Al, 0.3 to 0.5; Si, 0.3 to 0.5; C, 0.05. Chromium metal is manufactured in the electric furnace using either chrome ore, chromium chemicals, or a mixture thereof, with silicon as the reducing agent. Various grades of metal are produced, with the chromium content as high as 97 to 98 per cent and a maximum of 1 per cent iron and less than 0.20 carbon. Other grades are available carrying 87 to 90 per cent Cr, 1.25 iron, and 9 to 11 carbon.

Chromium metal is used in the manufacture of chromium bronzes, special alloys for tools, corrosion-resisting alloys, vacuum tubes, and certain alloys making up electric resistances.

Chromium-nickel Alloys.—Nonferrous alloys containing approximately 80 Cr: 20Ni are used in the manufacture of resistor elements for electric ranges, electric heaters, electric furnaces, and in other applications for resistors that must operate at high temperatures. The alloys are resistant to corrosion and may be obtained in the form of wire strips or ribbons.

Where the temperature of the elements does not exceed 1700°F., nickel-chromium-iron alloys containing approximately 60 per cent nickel and 15 per cent chromium find use. Where the temperature does not exceed 1200°F., a nickel-chromium-iron alloy

containing approximately 35 per cent nickel and 18 per cent chromium has been applied. Temperature-resistance curves of the above alloys may be seen in Fig. 1.

Hastelloy.—Hastelloy C is a nickel-tungsten-molybdenum-chromium-iron alloy, containing a maximum of 20 per cent Mo, 18 Cr, 6 W, 7 Fe, with the balance nickel, which finds use in withstanding strong acid oxidizing agents including nitric acid, aqueous solutions of chlorine, free chlorine, acetic, formic, and sulphurous acids. It also resists the oxidizing action of ferric or cupric salts.

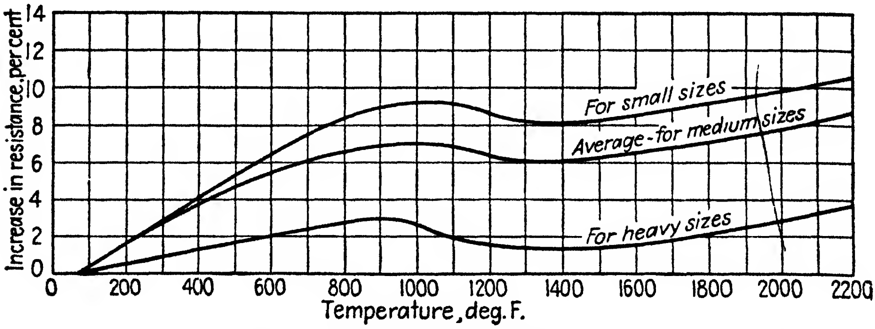

FIG. 1.—Temperature-resistance curve, Chromel A, showing effect of slow and rapid cooling.

The forms of Hastelloy available include castings, rolled sheet and plate, welded tubing and welding rod either for oxyacetylene or electric welding. The alloy cannot be worked either hot or cold, but castings are machinable at moderate speed. The characteristics of this alloy are listed below:

	Rolled and annealed	Cast
Ultimate tensile strength per sq. in.	115,000–128,000	72,000–80,000
Yield strength per sq. in.	55,000–65,000	45,000–48,000
Per cent elongation in 2 in.	25–50	10–15
Reduction in area	....	11–16
Hardness, Brinell, 3000 kg	160–210	175–215
Impact-Izod, ft.-lb	34–40	9–14

Stellite.—Stellite is a cobalt-chromium-tungsten alloy supplied in five grades. Stellite Alloy No. 93 is a high-chromium-cobalt ferrous alloy, containing chromium, cobalt, molybdenum, vanadium, and iron, which finds application where high cold-hardness is necessary and corrosion is not an important factor.

In hand-forming the Stellite may be applied by either oxyacetylene or electric-arc welding. Both bare and flux-coated rods are available for oxyacetylene and arc welding.

The use of hard-facing Stellite covers many varied industrial fields wherever wear is severe, such as mining, cement manufacture, automotive, aviation, excavation, machinery and equipment, and the iron and steel, lumber, and paper industries. Stellite in the form of high-speed cutting tools is employed in mass-production machining operations such as turning, milling, boring, and facing.

Chromium Steels.—The addition of chromium even in small amounts to steel subjected to heat-treatment results in greater hardness and tensile strength with little loss in ductility. In addition, a greater depth of hardening can be obtained

which is taken advantage of in the manufacture of armor plate and armor-piercing projectiles.

High-nitrogen ferrochromium is used in the manufacture of steels containing as much as 20 per cent chromium for reducing grain size and improving the physical properties. Chromium is also used for increasing the strength and hardness of cast iron.

Chromium is introduced into chrome steels in the form of ferrochromium, Chrom-X, or through the direct-reduction process. High-carbon ferrochromium is usually manufactured in a single-phase nontilting electric furnace with the electrodes submerged to as much as 2 ft. in the charge. The furnace burden consists of lumpy chrome ore, coal or coke, lime and fluorspar. The reaction is vigorous, most of the reduction occurring in the higher temperatures around the electrodes so that lumpy chrome ore is necessary in order to provide better heat distribution and avoid chimneying.

The power consumption in the manufacture of high-carbon ferrochromium is in the neighborhood of 3 kw.-hr. per lb. of chromium contained in the alloy, and the electrode consumption is 60 to 70 lb. per ton of alloy. Linings last 1 to 3 years without repair. Metallurgical efficiencies range between 80 and 85 per cent, so that approximately 2½ tons of 48 per cent chrome ore is required per ton of ferrochromium. The various grades of high-carbon ferrochromium carry between 66 and 70 per cent chromium, usually 66 to 68 per cent, with the carbon varying between 4 and 6 per cent. In addition, other grades of high-carbon ferrochromium are available for special uses where the carbon content runs as high as 10 per cent.

High-carbon ferrochromium is employed in the manufacture of armor plate, armor-piercing projectiles, gun barrels, piston rings, ball bearings, tool steels, and various other grades of chromium steel.

A process for the manufacture of low-carbon ferrochromium which has been practiced in this country for many years is a two-stage procedure. In the first stage chrome ore, usually fines, is mixed with quartzite, lime, and carbon to produce a chromium silicide low in carbon. The second step consists of adding lumpy chrome ore to the chromium silicide as a furnace burden whereby the chrome ore is reduced by the silicide to produce high-grade low-carbon ferrochromium. Other methods of low-carbon ferrochromium manufacture include a three-stage process in which a high-carbon ferrochromium is produced in the first stage and used as a raw material in the second stage for the production of chromium silicide. The third stage is the desiliconizing process as outlined in the above. Variations of the process include the manufacture of a chromium silicide containing approximately 40 per cent silicon. Chrome ore with lime is melted in the second furnace and the molten products mixed in a ladle. Approximately 5000 kw.-hr. is required per ton of chromium silicide and 1100 kw.-hr. for melting a ton of chrome ore. Approximately 1 ton of chrome ore is necessary per ton of chromium silicide, and the total power required is in the neighborhood of 6200 kw.-hr. per ton of ferrochromium. The electrode consumption ranges between 85 and 95 lb. per ton of ferrochromium. The chromium content of low-carbon ferrochromium ranges between 68 and 72 per cent with the carbon varying between 0.06 and 0.2 per cent maximum.

The principal use for low-carbon ferrochromium is in the manufacture of 18-8 low-carbon stainless steels of both the chromium and chromium-nickel types. The industries in which steels alloyed with low-carbon ferrochromium are utilized include the manufacture of turbine blades, cutlery, corrosion-resisting steels, decorative trim, acid-resisting metals, and electrical resistances.

Chrom-X.—The material known to the trade as Chrom-X is generally used as a ladle addition in the manufacture of low-alloy steels and iron. Two grades are manu-

factured—high-carbon and low-carbon. In addition to their use in the ladle, some grades can be used in the furnace or cupola. The material consists of a mixture of low-grade ferrochromium produced by direct reduction of low-grade ores with carbon, after which the ferrochromium is crushed and blended with ferrosilicon mixed with sodium nitrate and pressed into briquettes which are heated to a temperature just above the melting point of sodium nitrate. The nitrate forms a bond between particles and later supplies the oxygen for oxidation of the silicon and part of the carbon. The oxidation reactions are said to supply sufficient heat to melt the ferrochromium so that objections to the use of low-grade ferrochromium are thus eliminated. Typical analyses of high-carbon and low-carbon Chrom-X are given below:

High-carbon Chrom-X		Low-carbon Chrom-X	
Cr	46.5%	Cr	47.9%
Fe	29.0%	Fe	33.0%
C	7.2%	C	0.02–0.06%
Si	5.6%	Si	5.5%
$NaNO_3$	11.7%	$NaNO_3$	13.0%

Direct Reduction Process of Chromium Steel Manufacture.—An appreciable proportion of the stainless steel produced in the United States is manufactured by direct reduction process in the electric furnace with a burden consisting of chrome ore, stainless steel scrap, nickel scrap, carbon steel turnings or mill scale, ferrosilicon, and lime.

Chromium and Stainless Steels.—There are literally hundreds of different types of steels containing chromium, either with or without other alloying elements, which may be roughly grouped into three classifications: (1) low-alloy steels containing not more than 4 per cent chromium, (2) low-alloy steels containing not more than 4 to 11 per cent chromium, (3) chromium steels containing over 11 per cent chromium.

The chromium steels containing 1 to 4 per cent chromium find application where exceptional strength, hardness, and resistance to abrasion are of benefit such as in the manufacture of ball and roller bearings, car axles, grinding balls, and small metal working tools. Steel containing over 10 per cent chromium finds use in the manufacture of valves for internal-combustion engines, still tubes, high-temperature chemical equipment, and other uses where resistance to oxidation at high temperatures is present.

Stainless steels containing over 10 per cent chromium with or without 2½ to 25 per cent nickel and other elements in minor proportions possess, as well as an attractive finish, great corrosion resistance at high temperatures, high strength with high ductility and amenability to welding, drawing, or stamping, and have adequate machining properties—all of which render these grades of chromium steel of such importance that in the manufacture of stainless steel approximately 50 per cent of the total ferrochromium production in the United States is consumed therein.

Stainless steels find use in the aircraft industry, in the manufacture of ailerons, anchors, elevators, exhaust valves, struts and other structural uses, instrument parts, pontoons, and oil coolers. The building industry in normal times consumes stainless steels in elevator cages, exposed trim on doors, window frames and decorations, safety-deposit boxes, lighting fixtures, name plates, kitchen plumbing, kitchen utensils, and in many other varied uses.

The automotive industry uses stainless steel in the manufacture of carburetor parts, exhaust valves, and diesel engine liners, butterfly valves, gasoline engine pump parts, water pumps, radiator trim, and many other items.

The chemical industry consumes considerable quantities of stainless steel where corrosion conditions exist, particularly at high temperatures as in nitric acid and ammonia plants. The brewing, wine-making, food-packing, and canning industries are also users of stainless steel. Typical analysis of one type of stainless steel is given in the following: Cr, 17.5 to 20 per cent; Ni, 8 to 10; C, 0.08 to 0.20, Mn, 1.25; S and P, 0.03 maximum; Si, 0.75 per cent maximum.

Chromium Chemicals.—The principal chromium chemicals are sodium bichromate, sodium chromate, potassium bichromate, potassium chromate, and chromic acid.

The manufacture of sodium chromate, the first stage in the production of the other principal chromium chemicals, is carried out by roasting a mixture of pulverized chrome ore, soda ash, and lime in an oxidizing atmosphere in accordance with the following reaction, the lime serving to avoid fusion of the mix:

$$2FeCr_2O_4 + 4Na_2CO_3 + \tfrac{7}{2}O_2 = Fe_2O_3 + 4Na_2CrO_4 + 4CO_2$$

The calcine is leached with hot water and the liquor concentrated, from which the sodium chromate may be separated directly by crystallization. However, the solution is usually treated with H_2SO_4 and, after separation of the sodium sulphate so formed, is further concentrated to obtain bichromate of soda, which is the most widely used of all the chromium chemicals.

Typical analyses of the principal chromium chemicals are given below:

Sodium bichromate (sodium dichromate), $Na_2Cr_2O_7.2H_2O$; molecular weight, 298.05.

ANALYSES

	Technical crystal	Technical granular	Technical anhydrous	70% solution
$Na_2Cr_2O_7.2H_2O$	100.1%	100.2%	113.4%	70.0%
Chloride as Cl	0.05%	0.05%	0.05%	0.25%
Sulphate as SO_4	0.15%	0.15%	0.18%	0.30%
pH at 400 g. per l	3 8	3.8	4.1	

Sodium chromate (chromate of soda anhydrous), Na_2CrO_4; molecular weight, 162.00.

ANALYSIS (TECHNICAL GRADE)

Na_2CrO_4	99.0%
Chloride as Cl	0.01%
Sulphate as So_4	0.54%
pH at 200 g. per l	8.7

Potassium bichromate (potassium dichromate), $K_2Cr_2O_4$; molecular weight, 294.21

ANALYSES

	Technical crystal	Technical granular	Technical powder
$K_2Cr_2O_7$	99.9%	99.9%	99.9%
Chloride as Cl	0.05%	0.05%	0.05%
Sulphate as SO_4	0.01%	0.01%	0.01%
pH at 100 g. per l	3.7	3.7	3.7

Potassium chromate (chromate of potash), K_2CrO_4; molecular weight, 194.20.

Analysis (Technical Grade)

K_2CrO_4	99.8%
Chloride as Cl	0.05%
Sulphate as SO_4	0.10%
pH at 200 g. per l	9.2

Chromic acid (chromic anhydride), CrO_3; molecular weight, 100.01.

Analyses

	Technical flake, %	Technical powder, %
CrO_3	99.8	99.8
Sulphates as SO_4	0.10	0.10
Insoluble	0.01	0.01

Uses of Chromium Chemicals.—*Sodium bichromate* enjoys a great variety of uses in a number of industries. One of the principal uses of sodium bichromate is in the chrome tanning of leather whereby the treatment of the hides with sodium bichromate provides better wearing qualities, more flexibility, and greater resistance to heat and moisture than leathers treated by other methods. Sodium bichromate is also employed in the tanning of glove leathers and the preparation of furs. It is used in the textile industry as a mordant and also in the manufacture of dyes. Various cotton fabrics of the U. S. Army Quartermaster Corps are treated with sodium bichromate, which is also used for the processing of leggings, tents, and awnings for the U. S. Army. U. S. military uniforms and blankets are treated with bichromate of soda, and dyes for producing khaki contain this chemical.

Sodium bichromate bears a very important part in the pigment industry. Chrome oxide green manufactured from sodium bichromate is used for camouflage. Bombs, bomb trucks, and tractors are painted with chrome yellow. Chrome orange, a basic lead chromate, is used as a corrosion inhibitor.

Considerable quantities of sodium bichromate are consumed in producing films on magnesium alloys as well as in metal treatments, cleansing, pickling, red dip for brass, tin plating, and galvanizing.

Miscellaneous uses of sodium bichromate include the manufacture of wax and greases as well as various uses in the manufacture of airplanes, machine guns, and 75-mm. guns. Sodium bichromate is widely used to inhibit corrosion in air-conditioning equipment, refrigeration brines, air washers, coolers, condensers, automobiles, and diesel-engine cooling systems.

Sodium chromate is employed where alkaline conditions are required. It is used in refrigeration and automobile cooling systems as a protection against corrosion, and in the manufacture of pigments, textile finishes, photography, and the manufacture of dyes. Rocket grenades and tracer bullets also contain this chemical. Wood preservatives that are used for treating wood to be painted also contain sodium chromate.

Potassium bichromate may be substituted for sodium bichromate wherever the presence of potassium is preferred to sodium. It is the source of chrome in the manufacture of the double salt known as zinc chromate which is being widely used as a priming coat and protection against corrosion on steel surfaces exposed to the weather, including ships and steel structures.

Miscellaneous uses of potassium bichromate include photographic chemicals, manufacture of blue print paper, brake linings, aluminum rivets, refining of tungsten, and in specialized textile and leather finishes including glazed kid and ceramic colors.

Potassium chromate replaces sodium chromate where conditions require an anhydrous nonhygroscopic alkaline compound or the absence of sodium, particularly in medicinal and proprietary preparations. It is used in the manufacture of inks, and as a chemical reagent, and in the manufacture of certain ceramic and glass colors owing to its ability to distribute more evenly than neutral chromate of soda. Potassium chromate is also used in the manufacture of flux and metal-coating compounds including welding electrodes.

Ammonium bichromate has a place in photography, lithography, pyrotechnics, and the manufacture of certain oxidation and reduction catalysts.

Chromic acid is consumed principally in chromium plating and anodizing of aluminum and aluminum alloys, particularly in the aircraft industry. It is also used in the treatment of metal surfaces including etching, coloring, decorating, and as a protection against corrosion.

The mechanism of anodizing aluminum is a reverse process to that of electroplating, since contrary to the deposit occurring on the cathode, as in the case of electroplating, the film is formed at the anode and progressive oxidation of the base metal takes place beneath the anodic film, growing inward so that the last portion to be formed is next to the metal while the oldest part of the film is on the surface. This film is almost pure amorphous alumina.

Chromic acid anodizing is generally carried out in steel tanks containing chromic acid solution of 5 to 10 per cent concentration. Heating and cooling coils are provided to maintain the temperature of the bath at 95°F. plus or minus 5°. The portion to be treated is cleaned in a suitable alkaline detergent or solvent degreaser before introduction into the anodizing tank. These parts serve as the anode and the tank as the cathode. A low-voltage direct current is applied at the start, being gradually increased to 40 volts as rapidly as possible. After reaching 40 volts, the anodizing is continued for 30 min., followed by a dip in hot water, after which the parts are dried.

The film has excellent corrosion resistance and at the same time promotes a strong bond for zinc chromate primer. Aluminum anodized by the chromic acid process may be dyed with a variety of colored finishes[3]. Since chromic acid is itself an inhibitor, it is unnecessary to remove entrapped acid in preparation of priming. As a result, the chromic-acid anodizing process is the only process that may be used without restriction for all airplane parts made from alloys containing not more than 5 per cent copper, and considerable quantities of chromic acid are consumed for this purpose.

Chromium Plating.—According to Dubpernell[10], R. Bunsen[11] has often been credited with the electrodeposition of chromium in 1854, with the possibility that Junot[12] may have been successful as early as 1848. Many other prominent scientists worked on this problem, but none was commercially successful in the author's opinion until 1924 when Fink[13] developed and patented a practical method for chromium plating on a commercial basis. A chromium-plating industry soon developed using increasing amounts of chromic acid which amounted to a consumption of 9,000,000 lb. in 1937.

Chromium plating may be divided into two general classifications: decorative and industrial, or hard, chromium plating.

Chromium plate in thin coatings finds widespread use as automobile trim, for jewelry, metal furniture, and other similar uses where its attractive blue-white color and resistance to wear and corrosion are advantages.

Thin chromium deposits are inclined to have pinpoint porosity. For this reason, in decorative chromium plating, the chromium is deposited on an underlying coating of either nickel or nickel and copper. This type of plating is usually carried out at temperatures of 90 to 110°F. The thickness of the chromium plating for decorative purposes is usually between 0.00001 and 0.00002 in. Thicker deposits under the usual

conditions for decorative plating develop strains sufficient to start hair-line cracks unless special precautions are taken. Thicker deposits of chromium with little or no cracking may be obtained at 115 to 140°F. if the current density is in the lower part of the current-density range for the conditions chosen[14]. These higher temperatures are also selected for greater speed in plating in industrial applications.

Thick coatings of chromium plating, for convenience termed hard chromium plating or industrial plating, have found important places in many industries. Worn machine parts are plated to resize them, and small tools and gauges are plated to increase their life and wear-resistance. Chromium-plated surfaces have an exceptionally low coefficient of friction. This characteristic is used to advantage in the chromium plating of reciprocating parts such as pump rods, where the resistance of industrial chromium plating to corrosion is of additional benefit.

Diesel-engine cylinders are chromium-plated to reduce wear and friction and to protect them against corrosion. Gun barrels are chromium-plated to ensure accuracy over long periods of use. There are many other and varied uses wherein the hardness, corrosion resistance, and low coefficient of friction of hard chromium plating have been made use of.

The plating thickness is considerably greater than in the case of decorative plating, and where high resistance to corrosion is sought, relatively thick deposits of at least several thousandths of an inch are required[10].

Hard plating is usually applied to a hard basis metal such as hardened steel, the surface of which has been treated by electrolytic etching in order to assure a high adherence of the plating to the basis metal.

The source of chromium in the electroplating solution is chromic acid (chromic anhydride, CrO_3) which is manufactured in the form of dark-red flakes or powder with a specific gravity of 2.70, a typical analysis of which is seen on page 562.

The plating solution according to the inventions of Dr. C. G. Fink consists of chromic acid to which a catalyst acid radical has been added, usually sulphate or fluorides in an amount so as to maintain the ratio (by weight) of chromic acid to the total catalyst acid radical as expressed as sulphate at about 100:1. Sulphuric acid and sodium sulphate are widely used for this purpose.

The current efficiency in chromium-plating baths usually ranges between 10 and 13 per cent for bright plate, but owing to the relatively high current densities (100 amp. per sq. ft. and more) a rapid rate of deposition is obtained. Anodes are usually of lead or lead alloys, and plating tanks are usually acidproof brick- or lead-lined.

Two methods of preparing the surface for decorative plating are in use: wet cleaning and dry cleaning. The former consists of an alkaline cleaning operation followed by a water rinse and an acid dip. Dry cleaning involves mechanical treatment of the surface to be plated and is done either by buff wheel or by hand. The baths contain 250 to 400 g. per l. of CrO_3; 2.5 to 4 g. of sulphuric acid.

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CHAPTER XIX

THE METALLURGY OF MANGANESE

By Ernest A. Hersam[1]

Divisions of Metallurgy of Manganese.—The metallurgy of manganese becomes important under three separate interests of industry. Of these, the manufacture of manganese steel is perhaps first, being conducted on the largest scale, and requiring much of the manganese ore that is mined and which is smelted to reduce both manganese and iron. The second branch of the metallurgy is the concentration of the native manganese oxides and other minerals of manganese for use in the arts or further metallurgical manufacture, the enriched oxide being commonly useful as a coloring agent in the ceramic industry, as an agent to discharge the color imparted by iron in glassmaking, as a depolarizing agent in the manufacture of Leclanché and dry batteries, and for a wide variety of other but less important purposes. The third important use for manganese ore is in the preparation of chemical compounds that are of important service in medicine, in the production of electrolytic manganese, sanitation, manufacture, and other varied interests. The producer of manganese ore is compelled to follow all these divisions of the metallurgy to secure the proper marketing of his product.

Of the three divisions of the metallurgy, the first leads to the details of iron and steel manufacture, and is to be considered as a phase of the metallurgy of iron. The second, or ore dressing of manganese, which is the mechanical treatment of the ore, is identical with the mechanical enrichment of many ores other than manganese. In this division, crushing, sizing, and concentrating are adapted commonly to manganese oxides, which are of moderately high density, and in some cases of considerable magnetic permeability. Ore dressing is powerless to separate minerals beyond the state of natural purity in which the aggregates occur in nature. When, therefore, manganese minerals are intimately associated with earthy minerals, or with oxides of iron, infiltrated silica, or the carbonates of calcium or magnesium, no physical separation in the solid state is expected to render a satisfactory concentration possible Since this condition is a common one in the ore of this metal, hand sorting often is found to be the only treatment that is justified. The chemical treatment of the ore to purify the mineral or extract and deposit the manganese in chemical forms that can be employed in manufacture and trade leads to complex chemical relationships. These have to be understood in a broad way to master or to conduct practically the chemical treatment. The metallurgy of manganese, therefore, partly falls under this division.

The Commercial Production of Metal.—The commercial production of metallic manganese from the ore requires reducing smelting or electrolytic deposition. The reduction of the oxide to metal occurs at a roasting temperature without fusion, but the melting to produce metal of form suitable for most use demands costly smelting furnaces and presents difficulties exceeding the common ones of smelting. The manganese, upon smelting, is found highly volatile at the required temperature. A loss of 15 per cent from this cause is common experience. The manganese oxide, moreover, inclines to enter the slag.

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It becomes necessary, therefore, to smelt the ore at a high temperature, maintaining a strong reducing action throughout the operation, if smelting is carried on in the blast furnace. Such reduction results in the reduction also of all the iron, which collects in the metallic product. Thus, though a high content of manganese may be desired, an alloy of manganese with iron is obtained. Silicon, also, becomes reduced along with manganese in smelting, the amount depending upon the amount present and upon the character of the slag. Carbon, moreover, is inseparable from the product under the reducing conditions, and is present in the metal to the extent of 5 to 6 per cent. For these reasons it is not possible to smelt lean manganese ores with economy, nor, in fact, owing to the almost universal presence of iron and silica with manganese in ores, is it possible to produce pure manganese by commercial smelting. The best that can be done commercially is to produce a high-grade ferromanganese by the smelting. In smelting iron ore containing manganese to produce pig iron of 3 to 4 per cent manganese, the large amount of slag commonly occasions a heavy loss, carrying 3 per cent or more of manganese. This loss, together with the volatilization, makes it necessary to use ore of not less than some 9 per cent manganese to secure the recovery of this small amount of manganese in the product if desired. The production of a tolerably high-grade manganese product can thus be accomplished only by employing high-grade manganese ore and making provision in that case for receiving in the metallic product the entire iron content of the ore, which must then be held low. These conditions thus render it necessary to enrich the manganese minerals by hand sorting, or other ore-dressing methods if possible, before smelting. This is often a most unsatisfactory process, owing to the close association of the manganese minerals with barren and harmful minerals, limiting the commercial practice to ore of high grade. Electrolytic treatment will be discussed later.

Mechanical Enrichment.—An important part of the demand for manganese material is for the oxide or peroxide. From these oxides numerous refined chemical compounds of a varied nature are manufactured. In the supply of the oxides or chemical compounds the manganese may be recovered from the ore by chemical extraction and converted into the required forms by subsequent manufacture. For the purpose of chemical extraction a low-grade ore is sometimes used, but wherever mechanical enrichment directly permits of producing the desired final material, as, for example, manganese dioxide, the ore-dressing methods are greatly preferred. Often the manganese mineral is so closely associated with insoluble silicates as to render it practically impossible to recover it, either by ore dressing or by the processes of chemical extraction. Sometimes it is harmfully associated with alkaline-earth minerals which are soluble in the solvents for manganese. Even thus, when chemical extraction may be contemplated, mechanical enrichment as a preliminary step may be desirable.

In many cases, moreover, ore dressing may fail to produce concentrate suited to chemical extraction. Ore dressing, therefore, may be preliminary to (1) smelting to produce ferromanganese, spiegel iron, or low-manganese pig iron; (2) lixiviation to produce manganese oxides or other compounds; and (3) the preparation of various rough coloring ingredients for use in the manufacture of construction materials, or component for fertilizer or other uses. For all these purposes the principles of gravity concentration and magnetic concentration are applied.

The Minerals of Manganese.—The most valued minerals of manganese are the dioxides, of which *pyrolusite*, MnO_2, is the most important. It is a soft bluish-black or grayish-black mineral, 4.8 in density, containing combined water not exceeding generally 2 per cent, and containing, often, hydrous silica in combination or intimate association. *Polianite* is the anhydrous variety of this mineral, 5.0 in density, crystalline, and much harder. *Psilomelane*, corresponding also to the formula MnO_2,

is a grayish-black mineral, lustrous, massive, and hard, of 3.7 to 4.7 in density. It contains often much combined water, variable in amount, and usually also barium oxide, or potassium oxide, and sometimes the oxides of calcium or magnesium. *Wad* is the soft hydrous variety of the dioxide mineral. *Asbolite* and *lampadite*, and other minerals containing the dioxide of manganese, combined with oxides of other base metals, are known but are uncommon. *Hausmannite*, $MnO_2.2MnO$, of lower oxygen content than the above minerals, is a firm brownish-black mineral, 5.0 in density. *Manganite*, $MnO_2.MnO.H_2O$, is a gray mineral, somewhat softer, and 4.2 to 4.4 in density. *Franklinite*, (Fe, Mn, Zn)O.(Fe, $Mn)_2O_3$, is hard, black, and 5.07 to 5.22 in density. *Rhodochrosite*, $MnCO_3$, is the carbonate, pink in color, and 3.45 to 3.60 in density. Combined with iron or calcium carbonate, and sometimes with magnesium or cobalt carbonates, the mineral is given the name *oligonite*. *Rhodonite*, $MnO.SiO_2$, is the silicate, the manganese component of which sometimes is partly replaced by iron, calcium, or zinc, and which is reddish in color and 3.4 to 3.68 in density. *Braunite*, $3Mn_2O_3.MnSiO_3$, of brownish-black color and submetallic in luster, is 4.7 to 4.8 in density. Other silicates of manganese in combination with the silicates of the base metals are known but are rare. The sulphates and other native salts of manganese occur in nature but do not constitute working ores.

Manganese Metal and Compounds.—Manganese is notable for the diversity of its chemical forms. Varying in its state of oxidation from a bivalent element to a heptavalent one, it ranges from a basic-combining element at the one extreme to a highly acid one at the other, entering in its highly oxidized state into numerous acid forms or radicals. In its lower state of oxidation it resembles magnesium and ferrous iron. Somewhat more highly oxidized, it resembles aluminum and ferric iron. Still more highly oxidized, it acquires characteristics resembling titanium and sulphur. Finally, in the most highly oxidized forms, it resembles chlorine and other halogens. In its mineral state, and in its metallic comportment, it perhaps most resembles iron. The approximate similarity of its atomic weight, which is 55, with that of iron, which is 55.9, leads often to regarding the element as an equivalent in slags. The high native oxides, however, acquire a stable stage which iron does not attain. Many of the compounds of lower oxidation are strikingly similar to those of iron. In many cases these are isomorphous with those of iron, being inseparable by crystallization.

Metallic Manganese.—Manganese is a reddish-gray brilliant metal melting at 1230°C. and is harder and somewhat heavier than iron. It alloys with numerous metals and combines as iron does with carbon, but with greater avidity. It is attacked by acids with much greater energy than iron, and is dissolved rapidly by all ordinary dilute acids inclusive of acetic acid, evolving hydrogen copiously and producing manganous salts. It is oxidized by carbon monoxide above 330°C., and its affinity for sulphur and for oxygen at high temperatures is utilized in the metallurgy of iron for the deoxidation and desulphurization of that metal. The stability of the simple oxide renders it impossible to reduce and smelt the metal apart from metallic impurities, if present, and the affinity for carbon and metalloids at high temperatures renders it difficult to produce the metal by any pyrometallurgical means without contamination.

Manganese occurs in the allotropic forms as governed by temperature in heat-treatment. From the ordinary temperature of the air up to approximately 742°C. it is in the alpha form, and from 742 to 1191°C. in the beta form. In both of these phases the structure is cubic. Within the beta range at a temperature between 1067 and 1157°C. is found a discontinuity in magnetic susceptibility indicating changes not evident in the crystalline structure. Above the beta and at some temperature above 1191°C. the metal acquires the gamma form in which the structure is tetragonal.

These changes in phase become of great importance in the production and tempering of manganese steel.

Except for electrolysis, for producing the highly pure metal, the process of Goldschmidt, consisting of reduction by aluminum, best serves. For this reduction, a purified manganomanganic oxide is used as the source of the manganese, the aluminum powder being incorporated with oxide and raised in temperature to effect the reaction, sufficient aluminum being employed to produce sesquioxide of aluminum from the total oxygen content of the purified manganese oxide. Some 90 per cent of the metal may be so recovered without difficulty in a product of 96 per cent manganese free from carbon. Silicon, iron, and aluminum are the impurities of metal so produced, great difficulty being found in removing the final traces of these metals. Although chemically pure manganese may be produced under controlled electrolytic treatment from sulphates, chlorides, and other chosen electrolytes, the collection and fusion of the metal requires the extreme of attention to protect it from contamination with contacting elements of its environment.

Numerous processes are in existence for the production of metallic manganese of tolerable purity freed from much of the combined impurity with which the ore is generally associated. By the process of J. Y. Jones[1] manganese ore containing iron is finely ground, mixed with coal, and calcined at about 1090°C. with air excluded, to reduce the iron. The iron is removed, and the coked product is smelted to produce metallic manganese of grade according with the extent of the preliminary separation of the iron. Sternberg and Deutsch, as early as 1893,[2] produced metallic manganese by igniting the oxide of manganese when combined with alkaline-earth oxide at a temperature ranging from 1000 to 1200°C. in the presence of carbon. Other metals, such as molybdenum, tungsten, and titanium, were also included in the patent. Greene and Wahl, in 1895, prepared manganese, free from iron, by leaching the ore with dilute sulphuric acid to remove iron, leaving the dioxide of manganese unattacked. The purified material was then ignited to produce Mn_3O_4, followed by the application of volatile hydrocarbons in the treatment and a final reducing treatment with aluminum and magnesium in crucibles.

Ferrous Alloys.—Ferromanganese is the common commercial form of metallic manganese. In this alloy some 78 to 82 per cent manganese is present together with about 5 to 7 per cent carbon, and generally 0.5 to 1.0 per cent silicon with less than 0.03 per cent sulphur or phosphorus, the remainder being mostly iron. Humbert decarbonizes ferromanganese[3] by heating to a temperature above 1700°C. in contact with manganese oxide, in an electric furnace, reducing the carbon content thus to less than 1 per cent. Spiegel iron produced by blast-furnace smelting commonly contains 18 to 22 per cent manganese and 5 to 6 per cent carbon together with approximately 1 per cent silicon and small amounts of sulphur and phosphorus, the remainder being mostly iron. A lower-grade manganese product with iron is also produced by smelting iron ore when insufficient manganese is present to produce spiegel iron. In the production of metal of this type the tendency of the manganese to enter the slag, and the required maintenance of special smelting conditions to effect the recovery of the manganese, introduce costs that commonly detract from the economy of recovering this small proportion of manganese along with the preponderance of iron that also must be reduced. A German process effects a partial separation of manganese from iron occurring in ores, by reducing the mineral under delicately controlled conditions so as to produce metal from the iron oxide, leaving the manganese oxide unreduced. The reduced material is then smelted under conditions calculated to

[1] U. S. patents 1288422 and 1289790.
[2] English patent 13177.
[3] U. S. patent 1228925.

leave the state of oxidation unchanged, recovering the iron as metal, and the manganese as a rich slag suitable for the production of ferromanganese.

Nonferrous Alloys.—Manganese, which appears as an important component of numerous ferroalloys, is a less common component of nonferrous alloys. The manganese-gold alloy is brittle and gray in color, becoming yellow with gold exceeding some 90 per cent and forgeable at this higher percentage of gold. The composition of manganin, a useful alloy, calls for 12 per cent manganese, 4 per cent nickel, and 84 per cent copper. To the extent of some 2.8 per cent in brass, manganese effects a marked increase in the hardness and tensile strength. The introduction into bronze has been effected by various means as, for example, by alloying the ferromanganese with phosphorus and copper, and introducing this richer alloy into the mixture of the other metals. Manganese is made to alloy in small amount with copper and lead by adding the oxide with cryolite together with a reducing agent to the other metals in the molten state. When accompanying copper in commercially pure iron, manganese increases the effect of the copper, which in proper amount decreases the susceptibility to corrosion and decreases the red-shortness of the metal that is occasioned by the influence of the copper alone. In alloy with copper alone it imparts useful properties which are becoming better known and utilized. With 5 per cent of copper, or more, the quenched metal is malleable, and with 15 per cent, ductile, after quenching at 500°C. With 70 per cent copper the cold-rolled metal develops a tensile strength of 120,000 lb. per sq. in. In these alloys of varied proportions and generally of higher manganese there is a marked vibration-damping characteristic with influence upon magnetic susceptibility varying with the composition and heat-treatment. Alloys approximating 25 per cent manganese with 20 per cent chromium, the remainder being iron, are strong stainless metals adaptable to hardening and cold-working.

Manganese imparts very desirable qualities to magnesium alloys. The manganese is best introduced into them by the use of fluxes containing manganese chloride, the manganese being reduced from the flux by the molten magnesium. Iron is practically insoluble in magnesium-manganese alloys, and this fact is made use of in order to precipitate the iron out of magnesium.

Divalent Manganese Compounds.—Divalent manganese imparts a usual reddish cast to substances containing it. It is to be regarded perhaps as the most stable form in which manganese enters chemical compounds. The divalent manganous salts, for example, are distinguished from ferrous salts by not being susceptible to oxidization in acid solution by the action of the air when present. *Manganous hydroxide*, MnH_2O_2, is a pink precipitate produced by adding alkali to solutions of manganous salts. It is insoluble in an excess of the alkali, but dissolves in ammonia, changing, when thus alkaline, as it would do when neutral, to the brown manganic hydroxide by exposure to the air. Manganous hydroxide precipitated by ammonia in the presence of cyanuric acid develops unstable colorless crystals of a high polarizing power serving for microchemical recognition. *Manganous oxide*, MnO, is a greenish substance, obtained by calcining the carbonate or by precipitation from heated solutions of manganous salts. It may be obtained by the reduction of the higher oxides, but is with difficulty obtained free from other oxides. *Manganous sulphate*, $MnSO_4$, crystallizes with 7 molecules of water, and is analogous to ferrous sulphate. It also crystallizes with 5 molecules of water, being then analogous to copper sulphate. It crystallizes, moreover, with 4 molecules in characteristic reddish crystals. It yields monoclinic double salts with alkaline sulphates, of such composition as $K_2SO_4.MnSO_4.6H_2O$.

In 1894, A. R. Davis provided for the extraction of manganese in the form of sulphate from the oxide ore by means of ferrous sulphate, producing commercially

manganous sulphate by evaporation. By the process of C. Ellis basic manganese is converted to the sulphate by treatment with acid sodium sulphate. The formation of manganous sulphate in solution, from which the dioxide may be produced, is usually the first step in the treatment of the ores by hydrometallurgical extraction. This appears under Production of Manganese Dioxide from Ores, page 573. *Manganous dithionate*, MnS_2O_6, is formed by the action of sulphurous acid upon manganese dioxide in the cold. It is soluble in water and convertible into sulphate by oxidation. *Manganous carbonate*, $MnCO_3$, is a reddish precipitate when formed by the addition of alkaline carbonates to manganous salts. It is less susceptible to oxidation than the hydrate. *Manganous sulphide*, MnS, forms as a flesh-colored gelatinous precipitate from alkaline solutions by the action of alkaline sulphides. Precipitation from moderately strong hot solutions sometimes gives the precipitate the form of a greenish-gray powder. The sulphide is very readily attacked by the oxygen of the atmosphere or by any ordinary weak acid, yielding hydrogen sulphide and the manganous salt of the acid. *Manganese borate* is precipitated from manganous solutions by borax. As commonly prepared, it is in the form of a brownish powder. It possesses valued catalytic properties, notable use for which is in the acceleration of the drying of vegetable oils, which is a process of oxidation. It thus becomes an important component of commercial driers required in the paint and varnish industry, in which application it acts catalytically. *Manganese resinate* and *manganese linoleate* are also similarly serviceable in this use. In preparing the resinate, a rosin soap is first made by boiling rosin in caustic soda, which is then poured into manganous sulphate solution, producing a flesh-colored precipitate, which is the resinate. This is filtered, washed, and dried, being then soluble in hot linseed oil or in any one of a variety of organic solvents, such as chloroform. It is capable of being melted, and when cooled forms a brown mass that may be broken into lumps of similar solubility and suitable for handling. Four pounds of this material in 10 gal. of linseed oil give a quick-drying oil, leaving a glossy coat, or, when less is used, a pale drying oil. The linoleate is produced by boiling linseed oil with caustic alkali. This soap is then added to manganous sulphate or chloride, producing a brown mass which is subject to oxidation and which is readily soluble in hot linseed oil. One part of this linoleate mixed with five of linseed oil and poured hot into 10 gal. of oil at 250°C. produces a desirable drying oil.

Manganic Compounds.—The manganic compounds are much less basic in action than the manganous. In acid solution, the salt tends to become reduced to the manganous state. While in acid solution salts remaining unreduced are subject to marked hydrolysis, which results in the separation of *manganic hydroxide*, MnO_3H_3, from solutions approaching the neutral salts. The manganic hydroxide may be made readily to part with its combined water, forming a partly dehydrated hydroxide, manganite, MnO.OH, or the anhydride, Mn_2O_3, both of which occur in nature as minerals, whereas the hydroxide does not.

The preparation of pure *manganic sulphate*, $Mn_2(SO_4)_3$, or the *chloride*, $MnCl_3$, is rendered difficult by the tendency of the salt to hydrolyze, making it necessary, in preparing the sulphate, for example, from the oxide, to employ strong acid in the reaction, and rendering it difficult to remove the foreign salts from the paste of sulphate except by means of nitric acid. Manganic chloride also forms in strong solution, but is unstable when deprived of the excess of strong acid. The *fluoride* and the *phosphate* of manganese, in this state of oxidation, are red and violet in color and hydrolyze much less readily than do the other salts. These salts form double compounds with the alkalies, producing striking crystalline aggregates.

Tetravalent Manganese Compounds.—The perhydroxide of manganese, MnO_4H_4, is produced by the action of strong oxidizing agents on the alkaline or neutral hydroxide. For the purpose, chlorine, bromine, or hypochlorite may be used. It is a

dark-brown substance, amorphous, and reasily converted into a colloidal state. In this state of oxidation manganese formerly was employed extensively in the production of chlorine.

Thus when the perhydroxide is treated with strong cold hydrochloric acid, it dissolves, giving a dark-green manganic *perchloride*, $MnCl_4$. This salt hydrolyzes when diluted, producing again the perhydroxide, or decomposing into chlorine and manganous chloride upon warming. The perhydroxide, subjected to moderate dehydration without the presence of reducing agents, produces the partly dehydrated perhydroxide, $MnO(OH)_2$, which becomes peroxide on further dehydration. In producing chlorine from these compounds, a dioxide of manganese is treated with hydrochloric acid to produce the tetrachloride, which, upon elevated temperature, liberates Cl_2 and becomes manganous chloride, $MnCl_2$. The famous Weldon process consists in rendering this manganous chloride alkaline, with an excess of lime; in the presence of the excess of lime it becomes oxidized to calcium manganate, $CaMnO_3$, known as "Weldon mud," containing the manganese again in the tetravalent state suitable for further acidification with hydrochloric acid and the further generation of chlorine.

The *peroxide of manganese*, or *dioxide*, MnO_2, is unstable at elevated temperature and yields its oxygen to compounds capable of receiving it at that temperature. Thus, in the manufacture of glass, the peroxide discharges the green color of ferrous silicates by producing the less highly colored ferric silicate. Its presence assures a high state of oxidation of iron in ceramic material, imparting a brown or a violet color by the direct coloring action of the manganese oxide itself in silicate or other combinations. As a decolorizer for glass, manganese material of 80 to 85 per cent dioxide is commonly wanted, containing less than 1 per cent iron. Such material is used in glass to the extent of some 4 to 30 lb. to the ton of sand, in many processes of manufacture. While a siliceous ore is permissible for application to this purpose, the presence of carbonates is objectionable. For making glass in pits, powdered ore is used, while the ore in lump form may be used in some cases for melting larger masses. The dioxide is used direct as a drier for linseed and other drying oils in amount generally not exceeding 0.5 per cent. In this form it meets with the objection that it darkens the oil, to a greater extent than the sulphate, borate, oxalate, resinate, or linoleate. As a dyeing material for cotton the chloride is used, in many cases, as it imparts a brown color to the cotton fiber. Much manganese dioxide is consumed in the manufacture of manganates, chiefly in the production of the permanganates. The dioxide is reported to be converted into a colloidal form by adding concentrated ammonia to 0.5*N* potassium permanganate solution until the color becomes deep brown, resulting in a solution that remains stable in the presence of alcohol of any density.

Manganese Dioxide as a Depolarizer.—The peroxide of manganese as depolarizer for the manufacture of galvanic cells is of great importance. The physical form of the peroxide influences the effectiveness in a marked way, and the presence of soluble metallic impurity is of great injury. The largest consumption of manganese dioxide, outside that of iron manufacture, is to make use of this action in the manufacture of dry cells and other galvanic-battery elements. In this use the available oxygen, in excess of that required to constitute manganous oxide, governs the effectiveness and value. Freedom from metals that are electronegative to zinc, such as copper, nickel, cobalt, and arsenic, is especially important, copper being most objectionable. Such metals cause local corrosion on the zinc of the cell.

Caucasian pyrolusite of some 85 per cent manganese dioxide containing less than 1 per cent iron is commonly desired, yet ore of 70 to 80 per cent dioxide and 3 to 4 per cent iron is often used when suitable in other respects. Moderate hardness and a certain slight degree of porosity of the mineral are desired, even at the sacrifice of the

highest oxygen content. Sized, crushed material is employed which is commonly finer than 10 to 20 mesh. In the Leclanché cell, a depolarizing mixture of manganese dioxide with graphite is often used. The artificial dioxide free from acid and containing occluded moisture may be used with a low proportion of graphite.

A hydrated dioxide of manganese for depolarizing purposes may be prepared by the oxidation of dilute acid solutions of sulphates or chlorides, or by the treatment of the oxide with water, glycerol, and acid. In the process of A. A. Wells, dioxide for battery purposes is prepared by converting the oxide ore into carbide, treating in water to produce manganous hydroxide, and roasting in an oxidizing atmosphere containing steam. By the subsequent process of Ellis and Wells, dioxide, suited to the purpose, is made by permitting a hypochlorite to act on a slightly acid solution of manganous salt at about 100°C. A dioxide that gives a dead-black streak and is suitable as a depolarizer is produced under the process of Ellis,[1] by exposing manganous sulphate solution, containing not more than 10 per cent free acid, at a temperature near the boiling, to the action of chlorine. The precipitate is recovered and washed free from contaminating salts. The depolarizing material of batteries has been regenerated, by crushing the material, extracting the soluble salts by means of ammonium chloride solution, and reoxidizing the residue by treatment under pressure with hypochlorous acid or its salts, or by chloric acid.

In electrolysis, manganese salts incline to throw out the dioxide at the anode. This deposition ensues as a result of the hydrolyzation of the tetravalent manganese ion with a relatively complete breaking down of the hydroxide to the dioxide at the anode surface. The nature and the state of the cathode material influences the required e.m.f. in practical operation, which will be higher than 1.35 volts, the potential gradient between the dioxide and the manganous ion. In sulphate solutions, at the ordinary temperature of the air, deposition of the dioxide commonly occurs under an e.m.f. of approximately 2, the current efficiency decreasing with increasing acidity. At 70 to 75°C. practically 100 per cent current efficiency is secured. The decline of efficiency with increasing acidity does not prevail at this temperature as in the cold, thus permitting of the employment of 20 per cent acidity in extreme requirements.

Production of Manganese Dioxide from Ores.—The manufacture of manganese dioxide from ores consists in the extraction of the metal as a salt, held in solution at a low state of oxidation, and its release as dioxide by the agency of an oxidizing process. There are numerous processes of this type capable of operation with high efficiency and chemical completeness. These, however, are brought into competition with production from a varied supply of the native peroxide ore of a quality to permit the recovery by mechanical concentration of pure dioxide mineral for industrial use. Some of these chemical processes have long been known. Others have been stimulated by relatively modern interests and possibilities.

An early and important use, that has continued to be made, of the production of manganese peroxide is in the regeneration of calcium manganate, which may be regarded as a combination of the peroxide of manganese with calcium oxide. This appears in a step of the Weldon process, which at an early time was the only practicable process of cheaply manufacturing chlorine, already described. The Herrenschmidt and Constable process consisted in applying ferrous sulphate at the ordinary air temperatures to manganese ore for the extraction of the metal in the form of manganous sulphate, recovering also cobalt in a similar form, if present, and leaving the iron in the state of ferric oxide as a residuum in the vat, thus obtaining a manganese solution for such precipitation as is desired. In 1884, Readman secured an English patent for impregnating ore with a solution of ferrous chloride, heating in a suitable furnace to decompose the chloride, and forming the chlorides of manganese as well

[1] U. S. patent 1289707.

as nickel and cobalt, if present, relatively free from iron for the precipitation of dioxide.

The German patent of Nithack, issued in 1884, provided for spraying the dissolved chlorides extracted from ore upon hot inclined plates of fire clay in the presence of atmospheric oxygen, causing the release of hydrochloric acid and the production of an oxide of manganese of a lower state of oxidation than the dioxide. In 1884 an English patent was granted Herrenschmidt to use ferrous chloride solution as a solvent to extract manganese and nickel and cobalt, if present, from the finely pulverized ore, followed by the precipitation of the nickel and cobalt upon manganese sulphide, or hydrated manganese oxide, and recovery of the manganese sulphate by evaporation, or the oxide and hydrochloric acid by calcination. Further improvements of the Herrenschmidt and Constable process, in 1885, consisted in boiling the fine manganese or cobalt ore with ferrous sulphate, followed by decantation and oxidation of the sulphate.

The Dunlop process consisted in calcining the native or artificial carbonate of manganese to produce oxide of manganese, attempting a high state of oxidation by the calcining or roasting action, elevating the temperature to 300 to 400°C., and maintaining oxidation for 36 hr. in a special furnace in which the material was supported in small wagons with provision for their propulsion. M. A. Reychler shortened the duration of the roasting of the Dunlop process to approximately 1 hr., showing that 80 per cent dioxide could be obtained under the conditions. To destroy residual carbonate more effectively, Reychler moistened the manganese oxide ore with dilute nitric acid, allowing it to dry before calcining, whereby, at 125 to 260°C., nitrous fumes escape, accounting for some 10 per cent of the total nitric acid, and manganese dioxide of at least 91½ per cent purity is obtained.

By the Kuhlman process, nitric acid is applied in the calcining of the native oxide or carbonate, sufficient acid being used to convert all manganese to the form of nitrate before calcination. Campbell and Boyd in 1893 produced manganous carbonate, suitable for the Dunlop process, from waste sulphate liquors by precipitating with sodium carbonate solution, following by washing and drying. In the same year Albright and Hood used coal dust in conjunction with sulphuric acid in calcining manganese oxide to produce manganous sulphate to be recovered by subsequent aqueous digestion. The sulphate was converted to chloride by calcium chloride and the precipitated calcium sulphate separated. The chloride was then concentrated and the manganese converted to the tetravalent form of calcium manganate by the addition of lime and the characteristic oxidation of the Weldon process. Albright and Hood further developed the precipitation of manganese in the form of hydroxide from the sulphate solution by ammonia, recovering the excess ammonia upon evaporation and oxidation of the precipitated hydrate.

Chapman's process for producing manganese dioxide consists in roasting manganese carbonate with a chloride salt. By the process of C. J. Reed aqueous manganese sulphate is heated with nitrate salts, leaving manganese dioxide in the residue. By the process of Dutt & Dutt, the oxide ore and alkaline hydroxide are roasted at 600 to 750°C. in a current of air in a reverberatory furnace, producing manganate, followed by lixivating the roasted mass to remove iron as ferric hydroxide resulting from the reaction upon ferrites if present. The manganate solution is then decanted, evaporated, and heated in a retort to 500°C. in an atmosphere of steam, producing a resulting mixture of manganese dioxide and alkaline hydroxide, which is washed to remove alkali, and dried.

The Vadner process consists in bringing sulphurous gas from roasting sulphide ores, or produced by the burning of sulphur, into contact with manganese oxide ore of 5 to 35 per cent. This has been done by spraying the fine pulp into the gas. Silver

and base metal, such as zinc, are attacked and dissolved along with the manganese. Iron is precipitated by finely divided calcium carbonate, and the zinc is separated and recovered by precipitation with the like precipitant at a higher temperature. Finally, lime and air are used to precipitate the dioxide. A later improvement of the process consists in leading the pregnant manganese solution over manganese dioxide to precipitate lead and iron, and treating with chlorine to produce the dioxide of manganese. Zinc and lead are both recovered. The manganese produced never falls below 90 per cent manganese dioxide, and under the best conditions exceeds 99.5 per cent.

The process of Haslup and Peacock consists in digesting for 15 hr. or more the finely ground low-grade ore with added salts, such as ferrous sulphate, aluminum sulphate, or salts of potassium, that will contribute to the heat of reaction along with sulphuric acid not exceeding 55°Bé. The treatment is conducted in a heat-insulated container at a temperature of 150°C. The action of the free sulphuric acid is relied upon as the source of heat. In any case the temperature is developed and maintained by the reaction. The digestion is followed by the extraction of the sulphate in water in a condition suitable for conversion to the dioxide.

By the process of M. L. Kaplan, manganese carbonate is converted to the oxide by exposure to air containing nitric oxide at some 300°C. The decomposition product is recovered by heating the sulphuric acid solution containing it and which is passing from the oxidation chamber. The chief reaction of the oxidation is as follows:

$$MnCO_3 + NO_2 = MnO_2 + NO + CO_2$$

The lower oxide of nitrogen is converted to the higher state by the action of air. Provision is made for the treatment of native carbonate ore, or ore containing basic mineral, by the action of nitric acid, removing the excess of nitric oxide by the application of heat and producing dioxide suitable for battery purposes.

By the sulphurous acid process of Van Arsdale the manganese oxide ore, of 18 to 20 per cent manganese, reduced by crushing to 30 mesh, and containing water sufficient to produce a mobile pulp, is exposed to the action of sulphur dioxide as contained in roaster gas. The appliance that has been used for the absorption of the gas is the revolving cylinder of the Leaver type, with perforated disks and deflectors. Reaction occurs between the aqueous solution of the gas and the manganese oxide in accordance with one or both of the following reactions:

$$MnO_2 + SO_2 = MnSO_4 \quad (1)$$
$$MnO_2 + 2SO_2 = MnS_2O_6 \quad (2)$$

The treatment is required to be conducted at an elevated temperature, as with gases hot from the roasters. Reaction without this heating results in increasing the less desired effect indicated by reaction (2) above, which in any case cannot be entirely prevented. The dithionate of manganese produced by this reaction thus accompanies the sulphate produced by reaction (1). The treatment consists in a continuous and progressive digestion of the ore, or, when preferable, an intermittent digestion of identical action.

To obtain a manganese solution of high density, as, for example, 1.5 sp. gr., a progressive treatment of at least two steps is necessary, by which the depleted ore receives the action of the fresh gases entering, and the fresh ore imparts higher content to the effluent solution passing from treatment. Solution of density as low as 1.2 sp. gr. may be produced by either the direct or the intermittent procedure. Clarification of the solution resulting from the extraction of the ore is practically necessary, Oliver filters having been used with fair success on solutions of 1.2 sp. gr., or less. No practical way has been found to filter the stronger solution. The clear solution

from the treatment, following filtration, is evaporated to dryness in subheated cast-iron pans, expelling water and sulphurous anhydride from the dithionate and yielding a residuum of manganese sulphate. The firm adhesion of the salt to the pans requires mechanical removal, a chisel in an air hammer at times being required to detach the crusts. The dislodged and digested residue of manganese sulphate is calcined in a rotary kiln lined with magnesite brick, elevating the temperature at the heated end to 1950°F. or higher, and yielding manganese oxide, Mn_3O_4, in the form of nodules containing less than 0.5 per cent sulphur and of a high degree of purity. Manganese dioxide may be recovered from the heated solution also by electrolysis. By the process of E. H. Westling the economic production of manganese dioxide was conducted for a time at a plant of the American Manganese Products Co. at Redwood City, Calif., yielding manganese dioxide of a high degree of purity suited for industrial use, but on account of its form it was found less satisfactory in the manufacture of dry-battery cells than the pure dioxide mineral. The fine ore, containing dioxide and other oxides of manganese, was crushed to the 20-mesh size or finer, and thence elevated to storage tanks for an intermittent supply at a rapid rate of discharge. The thickened mobile material drawn from the storage tanks entered digesting vats of cylindrical form, provided with conical bottoms lined with acidproof brick bound with acidproof cement.

The digesting vats were provided with corrosion parts and with inner cylinders of a form resembling those of the Pachuca tank. Sulphur dioxide, with a slight excess of air, produced by the combustion of sulphur under pressure in a Schutte & Koerting burner, was conveyed, while warm, to the vat, and allowed to react upon the charge producing manganese sulphate. After digestion with the sulphurous acid solution and with air as described, the manganese sulphate solution and residues were conveyed to a tank where a little powdered calcium carbonate was added, to neutralize the solution and to precipitate iron and alumina, arsenic, and other impurities. This was done at about 50°C. under constant agitation. Following this treatment, calcium nitrate solution was added while agitation continued, resulting in the production of manganese nitrate, which remained in solution, and of calcium sulphate as a precipitate. The mass, consisting of manganese nitrate solution and residual insoluble material, containing the insoluble residue of the ore, ferric hydroxide, basic iron salts, and other mineral matter, contained also calcium sulphate crystals which coated the particles of the fine slime and rendered it easy of filtration. This residue was removed by filtration without difficulty by the ordinary Oliver filter.

Copper, when present in the ore and taken into solution by the action of the acid, was precipitated completely by aluminum dust, a separate precipitation treatment for which, when required, was provided. The clear solution of manganese nitrate, freed from copper and to a large extent from its original calcium salts, was evaporated in open pans, where all further and final separation of calcium sulphate occurred, producing crusts easy of removal. The evaporation was continued under pressure in vertical cylindrical retorts with conical bottoms provided with acidproof lining and corrosion parts. By this final evaporation treatment manganese nitrate decomposed, producing pure manganese dioxide and releasing nitric anhydride, which was recovered by means of scrubbing towers, in series, the first of which produced pure nitric acid of 1.38 sp. gr., used for the manufacture of lead nitrate. The more highly diluted acid recovered from the succeeding towers was brought to the required strength by systematic and progressive absorption of the nitric gases. The pure product was obtained in the form of an easily settled fine granular material that was readily washed, settled, dried, and recovered.

Much has been learned in recent years through investigation of the U. S. Bureau of Mines to aid our inderstanding of requirements necessary for treating some of the

large bodies of low-grade ores of manganese. Such treatment is necessarily specific in being suited to the region as well as to the variant character of manganese ores. Sulphurous acid, along with the minimum of required sulphuric acid, appears to be the best solvent. The extraction treatment is preceded by suitable and systematic ore dressing to govern the favorable fineness for processes of leaching or agitation. The fundamental purpose in this sulphurous type of extraction is to convert the higher oxides of manganese to the soluble sulphate by the action of sulphur dioxide, and to dissolve the protoxide content of the minerals, simultaneously, in sulphuric acid in proper dilution, which is either added as such, or is formed from the oxidation of the sulphur dioxide, and to leave unattacked, so far as possible, the iron oxide and other undesired components of the ore. The close association of the manganese oxide minerals with other components of the ores, including not only those of iron but also of calcium, phosphorus, silicon, aluminum, and other elements, requires the consideration, in practice, of many chemical and mechanical factors. Whatever the type of plant or the mechanical provisions for bringing the active, solvent agents into contact with the prepared ore, the countercurrent principle, by which the fresh ore first meets the nearly depleted solvent, is best applied. There enter also matters relative to the effectiveness of the degree of acidity of the solution in sulphuric and sulphurous acid, the temperature of treatment, the comminution relative to the character of the ore, the content of sulphur dioxide in the impregnating gas, the mechanical activity relating to solvent and ore grains, the duration of treatment, the selectivity of the solvent on the various desired and undesired minerals of the ore, the separation of tailing and of slime from the solution, the treatment of washings, and the avoidance of the development of manganese dithionate, during extraction, which entails added cost in recovery of unconsumed sulphur dioxide.

Manganese Oxide as an Interfering Mineral.—The extraction of silver, and in some cases of other metals, from ores in which the metal of high value is found in close association with the dioxide or other oxides of manganese has been notable for the difficulties that have been encountered. Attempts of many kinds have been made to separate the manganese or to render its influence otherwise negligible. Smelting the ore meets with no interference beyond that common to iron oxides, since manganese in moderate proportion enters slags in the form of oxide, or silicate, as iron would do. When metals are to be extracted by cyanide solvent, however, the interference is marked.

By the process of A. G. French, patented in 1913, manganiferous sulphide ores of zinc, lead, or silver are treated to recover the manganese by roasting at 700°C., followed by incorporating with the ore some 5 per cent of sodium bisulphate, and wet grinding, followed further by leaching, in which treatment sulphates of sodium, zinc, and manganese are extracted. The solution is subjected to electrolysis between anodes of lead and cathodes of zinc, at 2.5 to 4.5 volts and 200 to 300 amp. per sq. m. of cathode surface. The manganese content of the electrolyte is controlled to suit the conditions of deposition of the zinc, adding, when necessary, manganese sulphate produced by the action of aqueous sulphur dioxide of the furnace gases upon the manganese dioxide ore, using the spent electrolyte as an aqueous carrier of the sulphur dioxide from the roaster gases and as a solvent of the manganese yielded by the ore.

The Vermaes process[1] for the treatment of manganese-silver ores consists of a reduction roast in the presence of a chloridizing agent at a temperature below the volatilization temperature of silver chloride, followed by extraction with water and the recovery of the silver from the ore by cyanide. Carpenter's process for the treatment of manganiferous silver ores consists in a chloridizing-volatilizing roast at 1000°C., recovering silver from the collected fume and by the cyanide treatment of the residue.

[1] U. S. patent 1234426.

L. W. Austin has patented a process[1] which consists in adding raw pyrite with sulphuric acid to manganiferous silver ores, following by water washing and cyanidation. Many similar but minor expedients of varied sorts have been resorted to in the effort to obtain a satisfactory recovery of the precious metal from ore of this character.

Physical Properties of Manganese Dioxide.—The physical properties of manganese dioxide are well observed in the properties of the pure minerals which have been mentioned. It is, however, most difficult to obtain from any source a manganese mineral that may be said to be a dioxide of absolute purity. As a chemical precipitate, produced, for example, by the Westling process, the substance is a grayish-black powder, composed of hard and compact grains. The desired quality for depolarizing purposes and the existence of a colloidal form are elsewhere explained. The dioxide by recent experiment is found to be slowly acted upon by hydrogen or hydrogen sulphide at ordinary temperature and atmospheric pressure, resulting, in the one case, in the formation of a lower oxide of manganese and in the other of the sulphide of manganese. By the process of Clevenger and Caron, manganese oxide ores are treated to reduce the oxide to a lower state to facilitate recovering manganese by magnetic concentration.

Compounds of Hexavalent Manganese.—The hexahydroxide of manganese is not known, nor is the free acid corresponding to its partial anhydride (H_2MnO_4), which would correspond to manganic acid. The salts of this acid are known, however, and for the alkaline elements are stable and important under certain conditions. These salts are stable also in a state of alkaline fusion. In alkaline solutions they resemble the sulphates in comportment and with them they are in some cases isomorphous. When manganic salts are rendered neutral or acid, depriving the solution of negative ions to support the lower radical, the manganese passes into the heptavalent form and produces the well-known permanganate, a typical salt of which is permanganate of potassium, $KMnO_4$. In this transition from the hexavalent to the heptavalent form, an oxidizing action is implied, and a draft upon the action of some oxidizing agency is naturally made. When no agent is supplied, the manganic ion, MnO_4, is itself in part reduced, producing the dioxide (MnO_2) and yielding the oxygen required to produce permanganate. Nitric acid facilitates this reaction but does not amply yield the oxygen required. Chlorine and bromine are agents naturally suited to the reaction.

The prevailing color of the manganates is green, while that of the permanganate is violet. The transition from the violet to the green color implies always a change in the state of oxidation when it appears to follow the alteration of the acidity. The green or hexavalent form is highly stable at high temperatures and tends to take oxygen from any available source, as is the case when the dioxide is fused with alkaline hydrates. By its pronounced color it is a common evidence of the existence of manganese in fused mixtures. The alkalinity required for the existence of the manganate state in contact with water renders the salts important chiefly as transition products in the production or employment of permanganates.

Compounds of Heptavalent Manganese.—The ready transition of manganates into salts containing the heptavalent anhydride (Mn_2O_7), resulting in the formation of permanganate, is indicative of the stability of permanganate salts under normal conditions, and under conditions of acidity. In this form the manganese resembles the chlorine atom, which appears in corresponding combinations as perchlorate. Permanganic acid, itself, is stable in acid solution. It can be produced by decomposing barium permanganate with sulphuric acid, which removes the barium as an insoluble sulphate. The attempt to isolate absolutely permanganic acid results in producing the anhydride (Mn_2O_7), which is a violet-brown oily liquid,

[1] U. S. patent 1327974.

liable to explosive decomposition into oxygen and manganese dioxide. The reduction of permanganate, when employing it as an oxidizing agent, is thus different in result according to the relative presence of acid or base. In acid solutions, permanganates leave the dioxide as a decomposition product. In alkaline solution, the product is a manganous salt. Most substances, whether of mineral or of organic nature, that are conceived as being susceptible to oxidation are attacked and oxidized by permanganate in solutions or added to fusion mixtures.

The alkaline manganates and permanganates are produced in various ways, the principle of the treatment commonly being that of the oxidizing-alkaline fusion of manganese oxides. The action is commonly conducted in kilns by allowing air to react upon finely ground manganese dioxide and alkali. For ample yield and best results it is preferable to employ potassium hydroxide in an amount equivalent to 2.5 molecules for each molecule of the dioxide, maintaining a temperature of some 300°C., and supplying moisture with the air. By the process of Shoeld, the permanganate is produced from the manganate solution, of 1.15 to 1.2 density, by oxidizing electrolysis, using porous anode compartments. The Brewster process provides for the oxidation to permanganate by the application of chlorine to the hot solution. The patents of Lovelace, Lanning, and Judefind are for the production of sodium permanganate from sodium hydroxide by employing anodes of manganese containing tungsten, molybdenum, or silicon in anode compartments. James C. Adell makes use of the presence of the oxide of iron in an oxygenation treatment of alkali and manganese oxide in the presence of air. MacMillan accomplishes the reaction with the alkali by fine comminution of the mixture while at a temperature of 400 to 550°C. A patent of McCormack provides for mixing manganese dioxide with an aqueous solution of alkaline hydroxide, and evaporating the mixture to dryness, followed by a moderate elevation of the temperature to produce alkaline manganate. By the Vanderkleed process, sodium manganate is produced by the fusion of manganese dioxide with sodium peroxide.

Electrolytic Manganese.—The production of electrolytic manganese has a considerable importance for war industry; for the pure material produced by this process enables a close control of alloys that is otherwise impossible. In general the production of electrolytic manganese depends on the deposition of metal from an electrolyte carrying 34 to 36 g. per l. of manganese and 135 g. per l. of ammonium sulphate with about 0.15 g. per l. of sulphur dioxide.[1] The cathodes are made of 316 stainless steel, a semimirror finish being maintained on them by buffing every 4 days. If they are too rough, the manganese cannot be conveniently stripped; if they are too smooth, the manganese is likely to fall off in the cell. The anodes are 99 per cent lead, 1 per cent silver, 15 × 32 × ¼ in., drilled with as many 1⅜ in. holes as possible, which gives a higher anode current density than cathode and minimizes the production of manganese dioxide by an anodic deposition. The composition of the anode itself assists in keeping down the production of manganese dioxide. The anodes are surrounded by an 18-in. canvas sleeve, the lower end of which goes through a false bottom in the tank so that any manganese dioxide that is formed falls through the sleeve into the space between the true bottom and the false bottom of the tank. The diaphragms become clogged with calcium sulphate in about 4 to 6 weeks and must be discarded.

The electrolyte is fed into the space between the anodes and this canvas diaphragm and is depleted so that in the anode compartment there is 8 to 10 g. per l. of manganese.

[1] JACOBS, HUNTER, *et al.*, First Two Years of Operation of the Bureau of Mines Electrolytic Manganese Pilot Plant at Boulder City, Nev., *A.I.M.M.E. Tech. Paper* 1717, New York meeting, February, 1944.

The cathode current density is 45 to 50 amp. per sq. ft. The anode density, because of the holes in the cathode, is 81 to 90 amp. per sq. ft. The cell voltage is 5.0 to 5.3. After deposition for 24 hr., the cathodes are dipped in a 1 per cent solution of sodium or potassium dichromate, to prevent oxidation of the manganese. They are then washed in a separate tank and are dried and then stripped from the cathode by flexing and striking with a rubber mallet. 4.1 kw.-hr. produces 1 lb. of Mn.

The electrolyte is prepared by leaching manganese ores, in which the manganese has already been reduced to the bivalent stage, with spent electrolyte. Sulphuric acid and ammonium sulphate are added as needed to bring the composition of the electrolyte to the composition already given. The leach is neutralized with ammonia gas and freed from the barren tailings and the precipitated iron and aluminum hydroxides.

The neutral leach solution, in addition to ammonium and manganese sulphates, contains small amounts of iron, arsenic, copper, zinc, lead, nickel, cobalt, and molybdenum. These are precipitated by hydrogen sulphide gases, and the precipitate is taken out by filter pressing. The solution still contains a little colloidal sulphur, colloidal metal sulphides, and organic matter, which are introduced with the ammonium sulphate. A little ferrous sulphate is added and air passed in to oxidize the iron. This precipitates the iron as a mixture of ferric hydroxide and basic ferrous sulphate, which removes the sulphur and colloidals and also removes any residual arsenic and molybdenum.

The impurity that interferes most with the process is magnesium. It is necessary at intervals to refrigerate the electrolyte to 10 to 15°C., which throws out a triple salt of magnesium-manganese-ammonium sulphate. Fortunately this salt can be sold in the southeastern United States as a fertilizer. Some experimental work has been done on the precipitation of calcium and magnesium from the electrolyte by the closely controlled addition of ammonium fluoride.

The Hydrometallurgy of Manganese.—The wet treatment of manganese ore requires a knowledge of the manganese minerals and the compounds of manganese that appear in solutions, precipitates, minerals, and products. These matters have been discussed.

Considerable work has been done on the Wilson Bradley process, which depends on the reduction of manganese to MnO and of Fe_2O_3 of the ore to Fe_3O_4 at about 400°C. by a mixture of hydrogen, carbon monoxide, and water vapor. The calcine must be kept away from the presence of air in order to prevent reoxidation. It is then agitated with ammonium sulphate liquor at about 88°C. The manganese oxide dissolves as manganous sulphate with generation of ammonia gas. Apparently the difficulty of recovering the ammonia gas has been the chief obstacle to the general adoption of this process.

Another ammonia process was that of A. T. Sweet of the Michigan School of Mines. In this process manganese carbonate ore crushed to minus 65 mesh is mixed with ammonium sulphate and a little water and the mixed pulp roasted. This drives off carbon dioxide and ammonia, while the manganese carbonate is changed to sulphate. The sulphate is leached from the roasted pulp and the manganese precipitated by the ammonium carbonate recovered from the roast gases.

Ores that were low in lime and high in iron were treated by Prof. Sweet with sulphuric acid to produce soluble manganese sulphate, roasting the manganese sulphate to Mn_3O_4. So far as known this process has not reached the large pilot-plant stage.

Some rather promising results on manganese carbonate ores, specifically on those of the Chamberlain District, S. D., were obtained by leaching with calcium chloride. Prolonged digestion transformed the manganese carbonate into manganese chloride,

the calcium remaining in the ore as calcium carbonate. The manganese is then precipitated by calcium hydroxide, which regenerates calcium chloride for future use.

Manganese dioxide, as already indicated, is readily acted upon by sulphur dioxide, which dissolves the manganese as manganese sulphate. This furnished the basis for the so-called L. H. Ryerson process, also intended primarily to treat the carbonate ores of Chamberlain, S. D. It was purposed to use manganese sulphate solution as a catalyst for the oxidation of sulphur dioxide to sulphur trioxide and to use the sulphuric acid manganese sulphate solution as a leaching agent. The manganese sulphate not needed as a catalyst was to be calcined to manganese oxide and sulphur trioxide. On a working scale the oxidation of the sulphur dioxide did not proceed so rapidly as had been expected, which seemed to be the chief difficulty.

The Bureau of Mines also did some work on this problem, though the Bureau of Mines had the opinion that the sulphur dioxide leaching should be preceded by a sulphuric acid leach.[1] If a sulphuric acid leaching does not precede the sulphur dioxide leach there is a tendency to produce dithionates, which decompose on any attempt to concentrate the solution. It does not appear that this process passed the laboratory stage.

Nitrogen Dioxide Process.—Leaching with nitrogen dioxide has been experimented with by the Bureau of Mines.[2] The general basis for the process is the fact that manganese dioxide reacts with NO_2 and water to form manganous nitrate with 6 molecules of water. The oxidation of NO_2 to nitric acid was to be kept low by controlling the flow of NO_2 and eliminating air pressure. Under these conditions the nitrogen dioxide acts as a reducing agent on the manganese dioxide. Calcium and magnesium if present dissolve readily and can be removed only by crystallization. A pilot plant was to be erected by the Anaconda Copper Mining Co. to test this process on a large scale.

Manganese accompanying other metals is commonly freed by utilizing the permanence of its salts in acid solution in the presence of hydrogen sulphide, and the stability and insolubility of its sulphide in alkaline solution, iron being previously removed and thus not under consideration here. The manganese, therefore, accompanies zinc, nickel, and cobalt, from which, along with zinc, it is separated by the greater readiness of its sulphide to react with dilute acid. It is separated from ferric iron by the relative solubility of the manganous hydrate in ammonium chloride, and from zinc by the relative insolubility of the manganous hydroxide in alkali. The possible electrolytic deposition of the dioxide upon the anode of the electrolytic cell permits of separation from most other metals, lead being excepted, and, under certain conditions, silver.

Economic Demands.—The great demand for manganese arises in its metallurgical use as metal in ferroalloys and the industrial uses of dioxide and the several well-known compounds required in many varied applications. The production of the pure dioxide is seen to be a starting point for the manufacture of most compounds as well as for the preparation of the metal. Manganese minerals and products of low grade have been used for a wide variety of purposes, in some cases as coloring agents, as in the manufacture of terra cotta of required shade, or for cements and other construction materials. The use of manganese as a fetilizer has been shown by years of experience to have been helpful as a crop stimulant. The adaptability of ammonium-manganese-magnesium residues to use as fertilizers has been of immense aid to certain electrolytic manganese work. In medicine it is now known to be a stimulant of enzymes. Under present conditions, a low content of manganese in ores or minerals

[1] *U. S. Bur. Mines Repts. Investigations* 3649, July, 1942.

[2] *U. S. Bur. Mines Repts. Investigations* 3626, March, 1942.

signifies little value except where a high degree of concentration or a simple process of chemical extraction becomes possible.

Analysis of Manganese.—The chemical determination of manganese with assurance of accuracy in ores, or as a component of iron and steel, has been always an involved and exacting operation. Many methods are known, some of which have been shortened to become methods of convenient assay. The element, when present in iron and steel, commonly requires the longer procedure of quantitative analysis for accurate determination. One may read A. A. Blair on the "Chemical Analysis of Iron," or Sutton's "Volumetric Analysis." The zinc oxide method of Low[1] is commonly accepted as being well suited to ores. The method of Clennell[2] is suited to the determination of the manganese alloy with aluminum.

[1] *Cf.* Low's "Technical Methods of Ore Analysis."
[2] *Eng. Mining Jour.*, Vol. 105, pp. 407–410, 1918.

CHAPTER XX

COBALT

By A. B. Schaal,[1] M. J. Murphy,[2] and S. A. Laurich[3]

Occurrence.—Cobalt is found in igneous-rock formations in many localities widely scattered over the earth's surface. The individual deposits, while numerous, are small and usually in conjunction with, or part of, deposits of more abundant or more valuable metals, such as copper, lead, manganese, nickel, silver, and, occasionally, gold. Consequently, cobalt is usually produced incidentally to, or as a byproduct of, some more extensive metallurgical operation.

Some of the more important ores of cobalt are (1) smaltite, or tin white cobalt, $CoAs_2$; (2) cobaltite, or cobalt glance, CoAsS; (3) erythrite, or cobalt bloom, $Co_3As_2O_8.8H_2O$; (4) linnacite, or cobalt pyrites, Co_3S_4; (5) asbolite or asbolan, black earthy cobalt, an impure mixture of manganese and other metallic oxides; and (6) skutterudite, $CoAs_3$.

Of the many and widespread deposits of cobalt, the following have, or have had, considerable commercial importance: (1) the Katanga district, in Belgian Congo, where cobalt is found as a cobaltiferous copper ore; (2) Northern Rhodesia, where there is a similar deposit; (3) French Morocco, where smaltite is found in conjunction with gold, a rather rare occurrence; (4) Ontario, Canada, where cobalt occurs in a variety of forms in conjunction with the silver deposits around Cobalt, and with various nickel deposits; (5) Schneeburg, Germany, where it is found as smaltite, linnaeite, and asbolite, and is associated with silver, bismuth, and uranium. New Caledonia, which at one time furnished 90 per cent of the world's cobalt, has comparatively large deposits of asbolite. These deposits have not been worked much in late years, largely because others, notably those in the Katanga, can be worked more cheaply.

Other deposits, of more or less marginal and temporary commercial importance are found in Burma, New South Wales, South Australia, India, Norway, Sweden, Finland, Chile, Brazil, Peru, and the United States.

The most important deposit in the United States is that around Fredericktown, Mo., where cobalt is found as sulphide in conjunction with copper, nickel, and lead. This deposit has lately been revived, perhaps temporarily, because of world economic conditions. Some cobalt has been obtained recently as a by-product from the old iron mines at Cornwall, Pa. (see page 591).

In the first nine months of 1941, the last period for which such statistics are available, the following cobalt materials were imported into the United States:

1. From Belgian Congo: 6,631,692 lb. of "residue" (cobalt-copper-iron alloy) averaging about 41 per cent cobalt.
2. From Canada and Australia: 2,016,105 lb. of ores and "concentrates" averaging about 8.7 per cent cobalt.
3. From Canada: 484,800 lb. of cobalt metal.
4. From Belgium, Canada, and the United Kingdom, 38,002 lb. of oxide containing 70 to 71 per cent cobalt.

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These figures do not indicate usage, since much of the material, except the oxide, was brought in as preparation for the war emergency, especially item 1.

Until very recently (1944) the domestic cobalt deposits have not been worked, and to date (August, 1944) no refined material has been produced from these deposits.

Properties of Cobalt. *Physical Properties.*—Cobalt is a silvery white metal when polished, but is a gray powder when produced by reduction of its oxides. Its specific gravity is 8.756 for an unannealed sample, 8.81 for an annealed sample, and 8.925 for a swaged sample. It has a melting point of 1480°C. and a boiling point of 1900°C. Its atomic weight is 58.94.

There are two allotropic modifications of the metal. Alpha cobalt has a close-packed hexagonal lattice and is the stable form under 400°C. At 400° beta cobalt is formed. This modification has a cubic lattice. Both forms are known to exist below 400°C., but alpha cobalt is the stable form.

After iron, it is the most magnetic metal, and it retains its magnetism even at high temperatures.

It has a tensile strength of 34,400 lb. per sq. in. when cast, 36,980 lb. per sq. in. when annealed, and 100,000 lb. per sq. in. when rolled. Its compressive strength is 122,000 lb. per sq. in. when cast and 117,200 lb. per sq. in. after annealing. Its Brinell hardness varies between 124 and 130, but electrodeposited cobalt is harder than the ordinary metal, having a Brinell number that varies between 270 and 311.

Pure cobalt may be machined, but it is somewhat brittle. Its machining qualities are improved by the presence of small amounts of carbon which also make it possible to swage the hot metal.

Chemical Properties.—The hot metal combines with various gases. It decomposes steam at red heat. When finely divided, it ignites in an atmosphere of the oxides of nitrogen. It reacts with ammonia gas at 470° to form a cobalt nitride, Co_4N_2, which decomposes at 600°. At a pressure of 100 atm., finely divided cobalt reacts with carbon monoxide if heated to about 200°C., forming orange red crystals of cobalt carbonyl, $Co_2(CO)_8$. This reaction differs from that of nickel with carbon monoxide in that the latter reaction proceeds at atmospheric pressure and low temperature, and forms a basis for the separation of nickel from cobalt. It reacts with chlorine, bromine, and iodine to form the corresponding halide salts.

The metal is soluble in dilute mineral acids, forming cobaltous salts.

There are three oxides of cobalt, analagous to the oxides of iron. Cobaltous oxide, CoO, is a greenish gray; cobaltic oxide, Co_2O_3, is brown; cobaltoso-cobaltic oxide, Co_3O_4, is black. Solution of any of the three oxides in mineral acids results in the corresponding cobaltous compound.

$$CoO + 2HCl \rightarrow CoCl_2 + H_2O$$
$$Co_2O_3 + 6HCl \rightarrow 2CoCl_2 + 3H_2O + Cl_2$$
$$Co_3O_4 + 8HCl \rightarrow 3CoCl_2 + 4H_2O + Cl_2$$

Simple cobaltic salts do not exist, and if formed in solution, are probably immediately reduced to the cobaltous state. There are, however, many complex cobaltic compounds, *e g.*, potassium cobaltinitrite, $K_3Co(CN)_6$.

One of the most important methods of separating cobalt from nickel depends on the fact that, if cobalt is oxidized to the cobaltic state by means of chlorine, hypochlorites, or peroxide in neutral solution, the cobaltic salt formed immediately hydrolyzes and precipitates as cobaltic hydroxide.

Cobalt is precipitated in cold solution by dilute alkali forming a blue basic salt.

$$CoCl_2 + KOH \rightarrow CoOHCl + KCl$$

This basic salt is changed to the pink $Co(OH)_2$ on warming the solution. The precipitate, in turn, changes to brown $Co(OH)_3$ in contact with air.

Alkali carbonates produce reddish precipitates of variable composition.

The metal may be made from the oxide by briquetting the cobalt oxide with a carbonaceous material, or by passing hydrogen over Co_2O_3. Carbon monoxide slowly reduces Co_2O_3 above 500°C. and very rapidly at 900°C. or above.

A very pure form of cobalt metal may be obtained by heating cobalt oxalate, CoC_2O_4, at high temperatures.

Metallurgy.—Most of the cobalt is now produced from the cobalt-bearing copper ores found in the Katanga district of Belgian Congo. Treatment in blast furnaces on the ground brings the cobalt out in the slag. This slag, reduced in the electric furnace, forms a copper-iron-cobalt alloy, which, prior to the war, was refined largely in Belgium. Lately, however, this raw material has been shipped to Niagara Falls, N. Y., where a plant having a capacity of about 1300 tons of cobalt per year has been built by Electro-Metallurgical Corp. for the Belgian interests. This operation, like most of those dealing with cobalt, has been shrouded in secrecy.

This crude alloy has also been refined to cobalt salts and cobalt oxide in two or three Ohio plants, and at a New Jersey plant, whose processes are rather closely guarded. These latter plants are probably using wet chemical separations, whereas the Niagara Falls operation is at least partially electrolytic. The cobalt-copper-iron alloy has a fairly uniform composition. It contains about 1 to 3 per cent arsenic, 1 to 2 per cent silicon, and small amounts of nickel, lead, antimony, and manganese, totaling 2 to 3 per cent. The remainder of the alloy (92 to 94 per cent) is made up of iron, copper, and cobalt. It is usually divided about as follows: cobalt 40 per cent, copper 18 per cent, and iron 35 per cent. About the only published information on processing this material is contained in Thorpe's Chemical Dictionary.

Prior to 1941, cobalt was also produced from several other sources, notably in France, from Moroccan ores of approximately 12 to 15 per cent cobalt, 3 per cent nickel, and 45 to 50 per cent arsenic, and from the old New Caledonian sources. Cobalt was produced in Germany from smelter residues from Burmese antimonial lead operations, as well as Canadian smelter products, and local ores. It is certain that the German government subsidized these operations to enable them to compete in world markets. Some cobalt compounds were produced in this country for the ceramic trade, from Canadian silver-mine tailings enriched by small amounts of pick-mined higher grade material, making a "concentrate" containing 10 per cent cobalt, 3 per cent nickel, and 25 per cent arsenic together with iron, sulphur, and varying amounts of gangue.

During the last few years, some of the material formerly going to Germany and France was diverted to the United States, and some of the speiss from the antimonial lead operations in Burma was treated to recover cobalt oxide among other products. The cost of these materials is very high, and they cannot be cheaply treated.

Since 1941 an attempt was made to revive the Missouri deposits, and a plant was erected to concentrate the cobalt and nickel sulphides by flotation. These concentrates were roasted to remove most of the sulphur. The plant was also equipped to smelt these concentrates down to a cobalt-nickel matte, thus getting rid of a large part of the iron. The flotation concentrate ran 6 to 7 per cent cobalt. The roasted concentrate usually ran 12 to 15 per cent cobalt, while the matte, after roasting, usually contained about the same amount. Sulphur in the concentrate was quite high, but it could be roasted down to about 3 per cent.

Preparatory Treatment.—With the exception of the ores in Belgian Congo, nickel is almost universally associated with cobalt in amounts necessitating its separation. These ores are either oxides, sulphides, or sulphoarsenides of these metals, and usually

contain, in addition to iron and the gangue materials, varying amounts of copper, antimony, lead, and manganese.

Up to the present, cobalt must be separated from nickel by wet chemical means. Such methods are comparatively expensive, and the ores are usually concentrated by every available physical means, as far as possible, preparatory to wet chemical treatment. Tabling and flotation are both used for these preliminary concentrations.

Oxide Ores and Concentrates.—Two general schemes of treatment, after concentration by tabling or flotation or both, are applicable to this class of material. (1) It can be smelted and an alloy formed, cast into anodes, and brought into solution by electrolysis, or (2) it can be directly digested with muriatic or sulphuric acid. Both methods find application at present.

Owing to process difficulties encountered with sulphuric acid treatment, the metals are usually brought into solution as chlorides, or, after special preparation, leached with ammonium carbonate.

Sulphide Ores and Concentrates.—It is seldom that these materials are sufficiently soluble in sulphuric or muriatic acid to permit direct treatment with a view to eliminating sulphur as hydrogen sulphide. In the rare cases where this treatment succeeds, caring for the evolved gas constitutes a serious problem. To treat sulphide materials with an oxidizing mixture such as sulphuric acid and niter or muriatic acid and niter is usually impractical, owing to the difficulty of handling the heavy sludge of sulphur formed. It is usual, therefore, to roast off the sulphur as far as practicable, converting the metals to oxides, which are then subjected, after fine grinding, to acid treatment. Sulphur has been reduced to about 3 per cent by roasting, some sulphate being formed at the same time, not included in this figure. The roasting is done in multiple-hearth furnaces, and is a fairly cheap step.

Where large amounts of gangue and iron are present, it is perhaps preferable to smelt the sulphide concentrate down to a matte, removing the gangue and some of the iron in this manner. The matte is then crushed, ground, roasted, and pulverized, when it is ready for the acid treatment. The matte is usually made in reverberatory furnaces, oil fired.

Arsenical Ores and Concentrates.—Older methods of preparing such materials nearly always included smelting to a speiss, or a speiss and matte. In this way gangue is removed along with some iron, if the iron in the ore is high. Matte comparatively low in arsenic should then be roasted, as should speiss containing large quantities of sulphur. Where speiss is roasted, means must be provided for collecting the volatilized As_2O_3. Some arsenic will, of course, remain in the roast, care being taken to see that it falls to somewhat less than the iron content, to ensure its complete removal later in the process.

Some types of speiss, high in arsenic and low in sulphur, are probably best directly dissolved in acid, after grinding, without roasting, and the arsenic recovered as calcium arsenate.

Which method to use, *i.e.*, whether or not to roast a low-sulphur high-arsenic speiss, will depend on the local possibilities of atmospheric pollution, as well as the economics.

Several attempts have been made, prior to acid treatment, to convert the metallic constituents into such a condition as to provide selective solution, and thus partial separation, of the metals by the initial acid treatment. These attempts have been only partially successful. The appended references cover these trials, as well as complete processes which today possess only historical importance.

Preliminary Chemical Treatment, Unoxidized Material.—Two methods have been employed at this stage of the refining:

1. Smelting with soda ash, niter, and salt, on a cast-iron lining, at about 1300°F. The fluid melt is poured into a rapid stream of water and completely disintegrated. Arsenic passes into solution as sodium arsenate, sulphur as sodium sulphate. The metals, silica, alumina, and antimony remain in the residue. The slurry is filtered and washed. The arsenic is recovered as calcium arsenate. The cake is dissolved in muriatic acid, all metals passing into solution as chlorides. Sulphuric acid cannot be used where much gangue is present.

2. The finely ground material is digested with muriatic acid and niter in a glass-lined vessel, the nitrous fumes being recovered in an absorbing system as nitric acid, and re-used in the process. If the material is a high-arsenic low-sulphur *ore*, prolonged digestion is usually needed to bring about solution of the metals. In this case, the entire charge is placed in the dissolving kettle and heated with steam while agitating. If however, the material is a high-arsenic low-sulphur *speiss*, the finely ground material reacts instantly and completely with the hot oxidizing acid and is, therefore, fed into the acid in a stream at a rate that permits the collection of the fume in the absorption system and prevents the reaction from getting out of control. In the resultant solution, the metals are present as chlorides, the arsenic as arsenic acid, with more or less elementary sulphur, depending on the amount originally present. The following reaction typifies the behavior of arsenical ores:

$$5CoAs_2 + 12HNO_3 + 10HCl + 4H_2O \rightarrow 5CoCl_2 + 10H_3AsO_4 + 12NO$$

Oxidized Material.—After fine grinding, oxidized material is treated directly with sulphuric or muriatic acid, the choice being governed by two factors: (1) the physical condition of the material after acid treatment, with its effect on handling, and (2) the requirements of the subsequent separations. Usually solution in muriatic acid will be found advisable in the case of the more complicated materials. This is especially true since the present cost of muriatic acid is relatively low.

Usually, even if the material is finely ground, a considerable time, and heat, will be necessary to arrive at anything approaching complete solution. Residues, if they contain no important amounts of cobalt or nickel, are not removed after solution is finished, since they do not complicate subsequent steps.

Wet Chemical Separations. *Separation of Iron.*—From large amounts of iron, cobalt and nickel are probably best separated, in muriatic-acid solution, by neutralization with calcium carbonate to pH 3.0 to 3.5 and filtering of the resulting slurry. It will be necessary in most cases to use a filter aid such as sawdust, which is added after precipitation. At best, filtration and, especially, washing are difficult. It is probably advisable to repulp the cake with water, acidify to, say, pH 2.0, add more calcium carbonate to pH 3.0, and refilter. The whole operation should, of course, be carried out in a highly dilute condition. In the presence of much silica or alumina it may be necessary to raise the pH to 5.0. Arsenic, if present in an amount not more than equal to the iron, will be completely precipitated.

The presence of copper complicates matters severely. If the pH is 3 to 3.5 at filtration, most of the copper comes through and can be recovered, but at pH 5 a large proportion of the copper is precipitated.

In the case of lead, most of it will be retained in the cake, but much comes through, and will come down in the copper separation, later.

Antimony will remain in the cake, except, possibly, traces.

Separation of Arsenic.—So long as sufficient iron is present, arsenic will all be precipitated with the iron, probably as Fe_3AsO_4. It can be removed from the precipitate by digestion (hot) with caustic soda:

$$FeAsO_4 + 3NaOH \rightarrow Fe(OH)_3 + Na_3AsO_4$$

Copper also precipitates arsenic in about the same way as iron, probably somewhat as follows:

$$CuCl_2 + H_3AsO_4 + CaCO_3 \rightarrow CuHAsO_4 + CaCl_2 + H_2O + CO_2$$

Arsenic can be extracted from this precipitate with NaOH very satisfactorily, the reaction being probably

$$CuHAsO_4 + 3NaOH \rightarrow Cu(OH)_2 + H_2O + Na_3AsO_4$$

The extracted arsenic can be converted into calcium arsenate with very little trouble. This is being done commercially at present in at least one plant in the United States. The material started with is a speiss containing, in addition to cobalt and nickel, 2 per cent iron, 3 per cent sulphur, and 9 per cent copper, with 40 per cent arsenic. In this case it is evident that there is insufficient iron and copper to combine with the arsenic in the calcium carbonate precipitation. The metal deficiency is made up by adding copper hydroxide slurry. The whole is precipitated with calcium carbonate at pH 5 or a little less, filtered and washed on an Oliver filter. Most of the cobalt and nickel, and a little copper, pass into the filtrate. The cake is repulped with water, extracted with caustic soda, and again filtered and washed, the arsenic, except small amounts, passing into the filtrate. The cake from the caustic filtration is repulped with water, and run to storage tanks. This slurry provides the copper hydroxide added at the first precipitation. The volume of copper-iron slurry accumulates, and the excess over process needs is treated as follows: Muriatic acid is added to pH 0.5, when everything dissolves except antimony and some iron arsenate. Calcium carbonate is added to pH 3.0 when all the iron precipitates, carrying down any arsenic that has escaped the caustic extraction, and all but traces of lead and antimony. A little copper also comes down. Most of the copper and any cobalt and nickel remain in solution, which is filtered off and added to the first filtrate. The washed cake is discarded, or treated to recover antimony, if warranted.

Separation of Copper.—Copper has been separated from cobalt and nickel in various ways. From a concentrated sulphate solution properly acidified it can be done well by electrolysis. Most of the older chemical wet methods seem to have relied on soda ash or lime. These chemicals produce, at best, a very imperfect separation. Hydrogen sulphide in acid solution has been used, with success, but its use leads to hazards that cannot readily be overcome. Various other ideas have been advanced, most of which are impractical. Perhaps the best chemical method, which has found successful commercial application, is based upon the hydrolysis that takes place when neutral copper solution is agitated in the presence of air at about pH 6.0 or a little higher. The acid liberated is neutralized with calcium carbonate, and the reaction is fairly complete. The reaction takes place at room temperature and seems to be somewhat as follows:

$$3CuCl_2 + 2CaCO_3 + H_2O \rightarrow 2CuOHCl.CuCO_3 + 2CaCl_2 + 2CO_2$$

The actual product contains large, but not definite, amounts of CO_2. The air agitation frees the solution of CO_2 and carries the reaction to completion. If a complete removal of the copper is desired, a little excess of $CaCO_3$ must be used, which will, of course, remain in the final product. A little cobalt and nickel will be carried down, but these amounts are not important. It is not known whether this is due to coprecipitation or occlusion. In any case it is much less than where soda ash is used.

The success of this separation probably is due to the fact that at no time is there sufficiently high local or general alkalinity to cause precipitation of cobalt or nickel.

Lead is also carried down by this reaction, and is almost completely removed, probably as a basic carbonate.

The precipitate is granular and filters and washes with ease. The method is cheap and practical. The product when dried is light, fluffy, and highly reactive.

Copper is removed commercially by cementation on very finely divided nickel, prepared by reducing green oxide with charcoal. Probably cobalt would work equally well. Temperature for this cementation is given as 82°C. Copper has long been removed by cementation on scrap iron, but this has the decided disadvantage of introducing ferrous iron into the solution, and in the ultimate reckoning, is far from inexpensive. The resultant copper is in poor condition for recovery. It is usually smelted.

Separation of Cobalt from Nickel.—This separation is almost universally accomplished by exploiting in various ways one single fact. In neutral solutions cobalt is more readily oxidized than nickel. The oxidized cobaltic compound hydrolyzes and precipitates and is filtered off, leaving nickel in solution. The acid liberated by the hydrolysis, must, of course, be neutralized, to carry the reaction to completion.

Probably the earliest application of this reaction was the addition of bleaching powder and lime to the neutral solution of the chlorides (the classic Freiberg process).

$$2CoCl_2 + 4CaOCl_2 + 2Ca(OH)_2 + H_2O \rightarrow 2Co(OH)_3 + 3CaCl_2$$

In working with sulphate solutions, a mixture of sodium hypochlorite and soda ash or caustic soda was used.

$$2CoCl_2 + NaOCl + 4NaOH + H_2O \rightarrow 2Co(OH)_3 + 5NaCl$$

It has been done both hot and cold, but it seems fairly well established that above 40°C. nickel begins to react readily, and coprecipitate. In any event the separation is far from complete.

The procedure is about as follows: The hypochlorite is added to the mixture of the chlorides a little at a time and is stopped when the cobalt-nickel ratio is about 1:2 or 1:3, when appreciable amounts of nickel begin to precipitate. The solution is filtered, and the residue is washed, dried, and ignited to the oxide, largely Co_3O_4. This oxide, if the work is carefully done, contains 70 to 71 per cent cobalt and about 1.5 per cent nickel. The solution is treated further with hypochlorite and alkali, until no more cobalt remains in solution, when the slurry is again filtered.

Only nickel remains in the filtrate. The cake, cobaltic hydrate, containing nickel in considerable quantity, is redissolved in acid and added to a new batch.

It is further well established that this procedure succeeds only when the cobalt-nickel ratio in the original chloride solution is high, *i.e.*, perhaps 10 or 12 cobalt to 3 or 4 nickel, and in fairly dilute solutions. The lower the cobalt-nickel ratio, the less satisfactory is the separation, until in the case of about 1 cobalt to 3 nickel it fails completely. Probably the optimum concentration of cobalt plus nickel in the original chloride solution is about 12 g. per l. Where the cobalt-nickel ratio is low, the procedure is to precipitate the cobalt completely the first time, filter, dissolve, neutralize, and reprecipitate fractionally. This procedure, in certain cases, is insufficient and must sometimes be repeated to produce cobalt comparatively free from nickel.

A better separation was later accomplished by adding to the mixed chloride solution just enough calcium carbonate to neutralize the acid formed on hydrolysis of all the cobalt, and passing in chlorine gas until all the carbonate was dissolved.

$$4CoCl_2 + 2Cl_2 \rightarrow 2CoCl_3$$
$$2CoCl_3 + 6H_2O \rightarrow 2Co(OH)_3 + 6HCl$$
$$6HCl + 3CaCO_3 \rightarrow 3CaCl_2 + 3H_2O + 3CO_2$$

The solution is held at about 20°C. for best results. Much of the cobalt precipitates relatively free from nickel and is filtered off, dried, and ignited to oxide. The filtrate,

which is saturated with chlorine, is treated with calcium carbonate, whereupon the remaining cobalt precipitates, carrying down some nickel in the ratio of about 5:1. This precipitate is treated with acid to pH 3.5 and reintroduced into a succeeding batch. This method also succeeds better when the total concentration is low and the ratio of cobalt to nickel is high.

Herrenschmidt Separations.—The chloride or sulphate solution of cobalt and nickel is divided into two parts in one of which the cobalt and nickel are completely precipitated by hypochlorite, hot. The precipitate is filtered and the cake repulped with water. Both portions are heated to boiling, and, while agitating, the slurry is added to the clear solution. The following reaction takes place:

$$Ni(OH)_3 + CoCl_2 \rightarrow NiCl_2 + Co(OH)_3$$

The addition is continued until all the cobalt is precipitated, care being used not to add too much of the slurry. This separation is not very satisfactory, and usually has to be repeated several times to ensure even moderately good results.

Ferric iron can be satisfactorily separated from a cobalt or a nickel, or a combined cobalt-nickel chloride, solution by the addition of freshly precipitated $Ni(OH)_2$ or $Co(OH)_2$. This separation is successful if carefully controlled and the quantity of iron is not too great. Naturally the solution should not contain much free acid at the start (say pH 2). The iron will all be down at pH 3.5.

Copper can also be removed in this way, completely, but some cobalt or nickel or both will remain in the copper precipitate.

Recovery of Nickel.—Nickel remains in solution after the separation of cobalt. At this stage of the process it is usually associated with large amounts of calcium or sodium chloride or both, or, in the case of sulphate solutions, with sodium sulphate. Magnesium should have been carefully excluded from the process. Sulphate solutions can be concentrated and electrolyzed, and in some cases this may be desirable, especially if metallic nickel is sought.

Usually, it will be necessary to precipitate and filter off the nickel. If there is no calcium or magnesium present, the separation is usually made with soda ash; all the nickel is precipitated at pH 9. If calcium is present, either lime or caustic soda is employed, the end point being the same.

In any case, filtration is a problem. None of the continuous-type filters are suitable, and great difficulty is encountered using batch-type pressure filters. One of the most satisfactory installations for this purpose consists of a series of large rectangular tanks, each divided in the middle with a tight partition. Twenty-seven 6 × 6 ft. vacuum leaves are installed in each side of each tank. The leaves have bottom suction only, so they may be sucked dry.

The slurry is introduced into one side of the first tank, and vacuum is applied to build up a cake about ½ in. thick. The slurry is pumped to the other side of the tank, the volume made up with fresh slurry, and cake built up in the same manner. The cake on the leaves in the first side is sucked dry and washed down off the leaves with water at pH 9. It is repulped by violent circulation and drawn off into a catch tank. By this time the second side has filtered down, and the slurry is pumped back into the first side, the cake being treated the same as before. This provides a semi-continuous filtration, the slurry or pulp delivered to the catch tank containing about one-tenth the amount of salt present in the original slurry.

The slurry in the catch tank is run through a second filtration and repulping, the concentration of salts remaining being about 1/100 of that in the original slurry. This is repeated a third and, if necessary, a fourth time, when it is seen that if three cycles were used, the salt is reduced theoretically to 1/1000 of its original concentration, and if four cycles, to 1/10,000. Practically these ratios are not attained, but the washing is very satisfactory.

The resultant final slurry is run over drum driers and finally calcined to the oxide. Pulverizing is not necessary after calcining the drum-drier product. The drum-drier product itself is a light, highly reactive hydrate (or carbonate).

In one commercial operation, the calcined oxide is briquetted with suitable sticky carbonaceous material and reduced to metal in an electric furnace. The hydrate could be dissolved in sulphuric acid and electrolyzed. It could also be briquetted and reduced in an ordinary reverberatory, bearing in mind that nickel requires a comparatively high temperature for melting.

Another method of removing the salts from the nickel slurry is, of course, countercurrent decantation. This probably is quite practicable, but very large thickeners would be necessary, owing to the slow settling rate of the precipitate. The installation would be very expensive.

Cobalt Recovery at Lebanon, Pa.—The original ore as mined from the Cornwall ore banks is concentrated magnetically, giving 64 per cent of magnetite product (used as an iron ore) which still contains 1.73 per cent of pyrite and some cobalt. This cobalt is lost. There are 36 per cent of rejects, which carry 5.63 per cent pyrite and 0.0856 cobalt. This reject is treated by flotation after regrinding, giving a flotation concentrate weighing 5.92 per cent of the feed and carrying 88.7 per cent pyrite and 1.39 per cent cobalt. The cobalt recovery is 64.7 per cent in this process. A concentrate equal to 1.58 per cent of the reject, high in chalcopyrite, is taken off also. (The copper assay is not known, but the chalcopyrite concentrate carries 4.1 per cent of its weight in FeS_2 and 0.0623 per cent cobalt). The tailing from the flotation unit (92.5 per cent of 36 per cent) carries 0.41 per cent FeS_2 and 0.0062 per cent cobalt.

The pyrite-cobalt concentrate is burned at Baltimore for sulphuric acid, and the resulting cinder is then shipped to Wilmington, Del., where it is given a chemical treatment that recovers 80 per cent of the cobalt. The over-all cobalt recovery compared with the original content of the magnetite reject is 51.7 per cent.

The Uses of Cobalt.—Cobalt in the metallic state finds few applications because its properties are much the same as nickel, which is about one-fifth as expensive.

1. Cobalt can be drawn into wire that is stronger than either nickel or iron. It also has high corrosion resistance to salt solutions and alkalies.

2. In recent years, the alloys of cobalt have found greatly increased application. This is due to their high red-hardness, their wear resistance, and their magnetic properties. The most important alloys are as follows:

1. Stellite, a very hard nonferrous Co-Cr-W alloy used for cutting tools.

2. Carboloy, a tungsten carbide containing a large amount of cobalt, also used for cutting tools.

3. A Co-Fe alloy containing 35 per cent cobalt, used extensively as a magnet steel. New cobalt alloys developed especially for high magnetic permeability and retention are now available under the name Permalloy.

4. By replacing nickel with cobalt in the common nickel alloys it has been shown that cobalt has a markedly stronger effect on the desired property than nickel.

5. An alloy of 12 per cent Co and 85 per cent Al has a tensile strength 85 per cent above aluminum and a hardness 100 per cent above aluminum. It is resistant to the action of alkalies and organic acids.

6. Cobalt-base alloys are used as hard-facing welding rod and special cast and wrought products requiring resistance to abrasion or corrosion, such as burnishing rollers, bushings, dental instruments, cloth and rubber cutting knives, dies, homogenizing valves, refrigeration valves, centerless grinder rests, turbine-blade shielding, scientific mirrors, and parts for manufacturing dry batteries.

Compounds of Cobalt.—A large percentage of the total cobalt production is accounted for by cobalt oxide. Commercial cobalt oxide, Co_3O_4 assays about 70 to 71 per cent cobalt. The impurities depend on the method of manufacture and do

not usually exceed 3 per cent. A mixed hydrated oxide of cobalt and nickel containing small amounts of copper and manganese is satisfactory for enamel ground coats, and the difficult step of separating the cobalt and nickel is avoided. The ratio of cobalt to nickel in the mixed oxide is the same as it is in the starting material. Cobalt oxide is a necessary component of nearly all porcelain enamel ground coats. Although used in small percentages, it effectively promotes the adherence between the enamel and the metal. As a color oxide, cobalt produces a brilliant blue in ceramic material. With nickel oxide, and iron oxide, it produces black. Most blue oil paints contain cobalt.

Cobalt compounds have proved valuable catalytic agents in promoting oxidation reactions. Cobalt naphthenate, resinate, oleate, and acetate are important paint and varnish driers. In this instance, the cobalt in an oil-soluble form promotes the oxidation and polymerization of the drying oil in the paint to form a tough and dry film. Many organic oxidation reactions are carried out with the aid of specially prepared cobalt metal and oxide catalysts, usually in conjunction with other metals.

Some work has been done on cobalt plating which indicated that it is superior in some respects to nickel, but cost considerations rule against it. In addition, it oxidizes more readily than nickel and therefore is not suitable for heating appliances.

Cobalt compounds commercially available are as follows: cobalt oxide (71 per cent Co), cobalt naphtenate, cobalt sulphate, cobalt chloride, cobalt acetate, cobalt resinate, cobalt oleate. Some of the cobalt amines have recently found industrial application.

Electrolytic Cobalt.—While a good deal of secrecy is observed in electrolytic-cobalt operations, it is stated that electrolysis is carried on in a bath containing 200 g. per l. of Co as $CoSO_4$, 50 boric acid, 5NaF, at a current density of 25 amp. per sq. ft., using lead anodes and stainless steel cathodes.[1] The maximum allowable concentrations of impurities are Zn, 10; Cd, 1; As^{+++}, 3; As^{V}, 1; Sb, 10; Hg^{++}, 1 mg. per l. Up to 100 mg. per l. chromium is only slightly harmful and Ni, Cu, Fe, and Mn are not deleterious. Cobalt is recovered from the bath, when it becomes too depleted, by recrystallizing as $CoSO_4$ or as $CoSO_4.(NH_4)_2SO_4.6H_2O$, or by precipitating metals of the second group with H_2S under 20 lb. per sq. in. pressure at pH 4, followed by the familiar iron purification. It is said by another experimenter that the sodium fluoride can be replaced by sodium chloride and that platinum anodes are preferable to lead.[2]

It is also claimed[3] that cobalt can be commercially precipitated from a cobalt sulphate or chloride electrolyte containing high cobalt, at 100 to 200 amp. per sq. m. at 60 to 70°C., keeping the electrolyte neutral by $CoCO_3$. The current consumption is said to be about 2½ kw.-hr. per kg. of Co.

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[1] *Trans. Electrochem. Soc.*, Vol. 85.

[2] Personal correspondence.

[3] *Metall u. Erz*, Vol. 39, pp. 7–13, 28–32.

CHAPTER XXI

NICKEL

By Donald M. Liddell[1]

Ores and Deposits.—Nickel ores are of widespread occurrence throughout the world. They are found in almost every country of Europe, in Africa, India, China, South America, Cuba, and in various localities in the United States. The most important deposits, however, occur in Canada, New Caledonia, Norway, and Finland. Compared with the first two, the Norwegian deposits are relatively small, but were important during the World Wars, when all their production went to Germany. During the height of their prosperity, nearly 80,000 metric tons of ore containing approximately 1.20 per cent nickel and 0.50 per cent copper was treated per year.[2] The Finnish deposits which have been developed by the International Nickel Co. are the Kaulalunturi mines near Petsamo in north Finland near the Russian border, and it is reported that about 5 million tons of ore had been developed, carrying 3 per cent nickel, 1 per cent copper (*Mineral Trade Notes* 7839, 1940). It is also reported that nickel ore occurs in the southeastern part of Finland in the Nivala district, south of Oulu. The International Nickel concession has been taken over by the Russian government.

There are some recent developments in Brazil on which no exact information is obtainable, but these may also be important. The lateritic iron ores of Cuba, the Dutch Indies, and the Philippines may also be important future sources of nickel.

The existence of nickel ore in New Caledonia has been known since 1865, and the deposits have been worked since 1875. From the latter date until the end of 1915, about 2,245,354 metric tons of ore was exported.[3] Additional ore smelted on the island produced 26,368 tons of matte, containing about 45 per cent nickel. It is estimated that the contents of the ore and matte amounted to 156,394 tons of metallic nickel. During recent years the tonnage produced has declined rapidly. Previous to 1881 the ores produced contained from 10 to 12 per cent nickel, but since that time the grade has been steadily falling off until now it is about 5 per cent. In the 5 years 1916–1920 there were 76,113 metric tons of ore and 23,511 metric tons of matte exported. From the end of 1920 to the end of 1935, ore exports were negligible, but 72,492 tons of matte was exported. In the 4 years 1936–1939 about 29,000 tons of matte and over 106,000 tons of ore was exported. This of course was due to Axis stock piling. The ore may be assumed to have carried about 5 per cent nickel. Detailed figures have been published for the period 1927–1939 as to the matte tenor; 72,030 tons of matte exported in those years (included in the statistics given above) are said to have averaged 75.8 Ni. The New Caledonia ores consist principally of noumeaite or garnierite, a hydrated nickel-magnesium silicate, to which the formula $(Ni,Mg)SiO_3.H_2O$ has been assigned. The ore, as mined, contains 20 per cent or more of hygroscopic moisture, besides about 10 per cent combined water, and is dried

[1] Consulting engineer, New York.
[2] "Mineral Industry," p. 887, 1918.
[3] Report Royal Ontario Nickel Commission, p. 247.

before shipping. A complete analysis representing an average of the 7 per cent ore after drying at 100°C. is as follows:[1]

	Per Cent
SiO_2	42.0
MgO	22.00
CaO	0.10
Al_2O_3	1.00
Fe_2O_3	15.00
NiO	9.00
CoO	0.15
MnO_2	0.70
H_2O	10.00
	99.95

The absence of copper and sulphur is particularly noteworthy. The Canadian ores contain both, and to this fact is due the different methods of smelting and refining used. There is no information available as to whether or not the New Caledonia ore contains any of the precious metals. In any event, none are recovered.

The New Caledonia deposits of nickel are associated with a very basic rock which is now largely altered into serpentine. The nickel mineral is found in small veins in the serpentine and as concretions enclosing undecomposed rock masses. The garnierite is an alteration product, in which the nickel replaces the magnesia of the serpentine. When pure, the color is green, but the presence of iron causes a wide variation, passing through yellow and brown to almost black. The deposits are always found in the form of shallow beds on the slopes of spurs from the main mountain range of the island, and at elevations of 400 to 2500 ft.

By far the most important deposits of nickel known at the present day are those of the Sudbury district, Ont., Canada. Nickel ores have been discovered at a number of points in Canada, but from two only, besides the deposits of the principal district, has there been any production. These are the Alexo mine on the Temiskaming & Northern Ontario Ry., near Matheson, Ont., which shipped ore for a number of years to the Mond Nickel Co.'s smelter at Coniston, and the Cobalt silver district, where nickel, chiefly in the mineral niccolite, is found associated with the silver, and is recovered as a by-product at the various plants where the silver bullion is produced.

The ores are closely associated with a pre-Cambrian intrusion of noritemicropegmatite rock, which encloses an oval-shaped area of later sedimentary rocks. The longer axis of the oval lies in a northeasterly-southwesterly direction and is about 33 miles in length. The width is about 13 miles. The enclosing norite ring, which is acid in character toward the inner part and shades to a basic composition as it approaches the outer edge, has a varying width of 2 to 4 miles. Most of the known deposits are found at the outer or basic edge of the norite, but some important ore bodies known as "offset deposits" have been worked at a distance of several miles from the basic edge.

The ore consists mainly of magnetic iron pyrites, or pyrrhotite, always mixed with more or less rocky matter or gangue, but often remarkably free from it and then massive and close grained in appearance. Various formulas have been worked out for the pyrrhotite, but, on the whole, it corresponds very closely to Fe_8S_9. Copper, in the form of chalcopyrite, $CuFeS_2$, is always present, frequently in sufficient quantity to be easily distinguishable by the eye. The nickel mineral, however, is so intimately associated with the pyrrhotite that, in general, nothing short of a chemical analysis will

[1] "Mineral Industry," p. 862, 1918.

establish its presence. By the use of a magnet on the finely ground ore from selected specimens free from copper, and by the exercise of a good deal of patience, it is possible to separate the ore into a magnetic and a nonmagnetic portion. The former will consist of barren pyrrhotite, while the latter will be the nickel-bearing mineral. Careful work of this kind has shown the nickel mineral to be pentlandite,[1] $(Ni,Fe)_{11}S_{10}$, containing Ni 36.0 per cent, Fe 30.4 per cent, and S. 33.6 per cent. Another nickel mineral, polydimite, Ni_3FeS_5, is met with in some of the mines in readily distinguishable masses, but, although such occurrences are very rich in nickel, polydimite is of secondary economic importance. Of interest only mineralogically are such minerals as millerite, NiS, niccolite, NiAs, and gersdorffite, NiAsS, which are found occasionally.

All ores mined contain, in addition to the copper and nickel, small amounts of the platinum-group metals, as well as a little gold and silver. These metals are concentrated during the smelting operations and are collected in the matte which goes to the refining process. No reliable analyses are available of the precious-metal content of the ores, but the following analyses[2] of two samples of converter matte, 1 ton of which represents 15 to 25 tons of ore, indicate that the amounts present in the ores are small:

	Ounces per ton	
	No. 1	No. 2
Gold	0.027	0.256
Silver	1.840	6.155
Platinum	0.1235	0.988
Palladium	0.197	0.984
Iridium	0.046	0.065

Though the amount of the precious metals in the ores is not large, their recovery from the matte makes the International Nickel Co. the world's greatest source of the platinum-group metals.

The gangue rock associated with the ore is, in general, of two kinds, acid and basic, with the latter predominating. The acid rock is mainly granite from the foot wall. The norite forms the hanging wall and some is found mixed through the ore, as is also an associated greenstone. The analyses[3] at the top of page 596 are the averages of a number made on each kind of rock.

The ore as shipped from the mine seldom contains less than 30 per cent rock, and may have 50 per cent or more.

Smelting of New Caledonia Ores.—The recovery of the nickel from the New Caledonia ores, which contain no copper, sulphur, or other element that might be expected to add to the difficulty of treatment, would, at first glance, appear to be a simple matter. The method of treatment originally proposed was to mix the ore with limestone to flux the siliceous gangue, and smelt the mixture with sufficient coke to reduce the nickel and furnish the necessary heat to produce liquid slag. The removal of the gangue as a molten slag could be accomplished readily enough, but the reduced metal or "fonte," containing about 65 per cent nickel along with considerable iron, proved difficult to deal with. It could not be bessemerized directly while still liquid, nor would it easily be broken up for further treatment after it had solidified. Moreover, as the coke used always contained a certain amount of sulphur,

[1] Dr. C. W. Dickson.
[2] Report Royal Ontario Nickel Commission.
[3] Coleman, A. P., "The Nickel Industry."

	Per cent	
	Acid	Basic
SiO_2	67.862	52.770
Al_2O_3	12.688	18.943
Fe_2O_3	1.740	0.283
FeO	5.072	9.140
MgO	1.164	4.940
CaO	2.468	7.617
Na_2O	3.956	2.597
K_2O	2.780	1.330
H_2O	1.050	1.263
TiO_2	0.456	1.097
P_2O_5	0.178	1.300
MnO	0.036	
	99.452	99.760
Specific gravity	2.718	2.897

and as this was taken up with avidity by the reduced nickel, it precluded the use of the fonte directly as ferronickel. The absence of the sulphur in the original ore proved to be only an apparent, and not a real, advantage. When these facts came to be recognized, the method now in use was adopted.

The present treatment is based on the production of a matte by adding suitable fluxes and sulphur-bearing material of some kind. Gypsum is the usual source of the sulphur, but alkali waste, chiefly calcium sulphide, or even pyrite may be used. It is customary to briquette the ores with the necessary fluxes and any flue dust that is recovered. The briquettes,[1] after air drying, are smelted with 33 per cent coke in water-jacketed furnaces, producing a matte containing between 30 and 45 per cent nickel, and a slag assaying 0.30 to 0.40 per cent nickel. The furnaces originally used had a capacity of only about 20 tons per day, but the larger ones now operated have a capacity of 100 to 120 tons per 24 hr. The following analyses give the composition of the furnace charge and the resultant slag.[2]

	Per cent							
	SiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	CaO	SO_3	H_2O
Ore	41.50	....	.....	9.19	20.22	....	...	8.11
Briquettes	37.40	3.5	.....	11.15	18.20	3.5	5.7	10.12
Slag	45.50	8.12	10.12	.....	17.22	9.14		

The matte produced in the smelting operation is bessemerized in small converters, a siliceous flux being added to slag off the iron oxide formed. The product from the

[1] GOWLAND, "Non-ferrous Metallurgy."
[2] Report Royal Ontario Nickel Commission.

converters contains approximately 80 per cent nickel and 20 per cent sulphur, with the iron usually not over 0.25 per cent. It is next ground in ball mills to pass through 60 mesh and then roasted till free from sulphur, giving practically pure nickel oxide, which may then be reduced to metal by means of carbon or other reducing agent. The nickel oxide and the reducing agent are ground together and briquetted into either "rondelles," circular disks about 2 in. in diameter and 1½ in. thick, or ¾-in. cubes, to meet the requirements of the market. The reduction is carried out by heating in horizontal retorts to bright redness for about 48 hr. The rondelles or cubes, when ready for the market, contain about 99.25 per cent nickel.

Canadian Smelting.—There are three Canadian plants treating nickel ores: Copper Cliff, which produces a blister copper for refining to electrolytic copper and an impure nickel to be refined to pure nickel or to nickel oxide. Coniston, the old smeltery of the Mond Nickel Co., which produces nickel matte serving as the raw material for Monel metal and white metal which goes to Copper Cliff for separation of the nickel and copper. Falconbridge, which normally sends its matte to Kristianssand, Norway, to be refined by the Hybinette process, but which is at present shipping its product to be refined by the International Nickel Co.

The International Nickel Co., Ltd.—The latest practice described[6] is based on crushing all the ore and giving it a bulk rougher flotation, which recovers about 95 per cent of the copper and 85 per cent of the nickel. The rougher concentrate is then cleaned selectively three times, splitting it into a final copper concentrate, carrying about 1 per cent Ni, and a final nickel concentrate. The tailings from the first rougher flotation are given a final flotation, which produces an impure concentrate that is cleaned from silica, the cleaned concentrate being added to the final nickel concentrate. The entire flotation tailing is finally tabled, by which some arsenides carrying precious metals are recovered. This arsenide concentrate is also added to the nickel concentrate.

Nickel Concentrate Treatment.—The nickel concentrate is roasted in Herreshoff furnaces, one being placed over the burner end of each reverberatory in which the smelting is done. These reverberatories are 110 × 24 ft., and the feed is 82 per cent calcines, 15 per cent sand, and 3 per cent scrap. All exhaust gases are passed through Cottrell precipitators, and the recovered dust is returned to the reverberatories. The matte from this reverberatory smelting goes to 13 ft. diameter Peirce-Smith converters. These are fluxed with barren sand, blown in with a Garr gun, and the charge is blown to "white metal." The product runs approximately 48 per cent Ni, 27 per cent Cu, 2 per cent Fe, and 23 per cent S and goes to the so-called Orford department, for top and bottom smelting to separate the nickel and copper.

Top-and-bottom Smelting.—The white metal from the Peirce-Smith converters is smelted with sodium sulphate and niter cake in cupolas 198 in. long and 48½ in. wide; the flux is reduced to sodium sulphide in which copper sulphide is much more soluble than is nickel. The fused product is allowed to solidify, the lighter copper sodium sulphide forming the "first tops," which carry about 40 per cent Cu and 4 per cent Ni, and the heavy nickel sulphide forming the "first bottoms" (approximately 65 per cent Ni, 9 per cent Cu). When cold, the tops and bottoms separate readily.

These first bottoms are again smelted with niter cake or sodium sulphate, the second "tops" running about 15 per cent Cu, 12 per cent Ni. These are returned to the first smelting. The second bottoms contain about 72 per cent Ni, 2 per cent Cu, and go to the nickel-recovery plant.

The first tops, containing the bulk of the copper, as already indicated, are bessemerized in Peirce-Smith converters, 10 ft. in diameter, 35 ft. long, with blast at 16 lb. pressure. The sodium sulphide oxidizes to sodium sulphate, in which neither

copper nor nickel sulphide is soluble, the sulphate going back to the smelting furnaces. During this blow the converter should be run below the temperature at which either sodium sulphate or sodium sulphide is volatile, which results in the accumulation of some heavy-metal scoria in the converter.

The copper sulphide after it is freed from the sodium sulphide is transferred to clay-lined converters where it is overblown to free it from nickel. The blister,

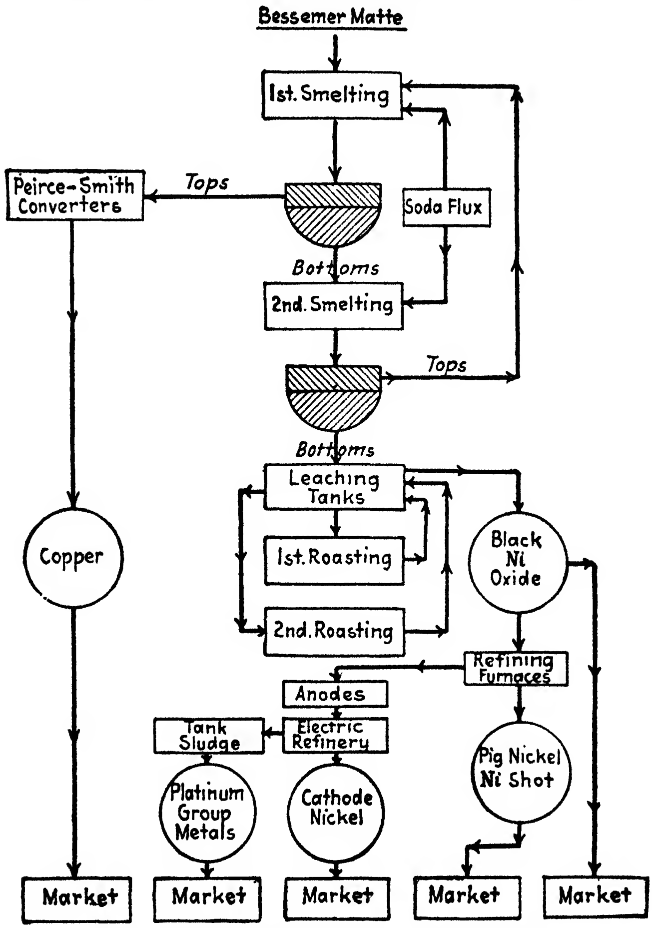

Fig. 1.—International Nickel Co.'s flow sheet.

saturated with Cu_2O, goes to the copper refinery, while the high-nickel converter slag goes back to the nickel reverberatories.

Coniston Plant.—The Coniston Plant is that formerly owned by the Mond Nickel Co. and is about 8 miles east of Sudbury. At the time of the latest authoritative information concerning it[6], it had six sintering machines, four blast furnaces, and five Peirce-Smith converters. The ore treated is a coarse magnetic ore from the Frood mine, and magnetic ore from the Creighton mine, both coarse and fine. The high-grade matte from the Creighton ore, carrying about 2Ni:1Cu, is shipped to the International Nickel Co.'s plant at Huntington, W. Va., for the production of Monel metal. The high-grade matte from the straight Frood ore or from the mixture of Frood and Creighton ores goes to the Orford plant, described above.

The sintering machines are 42 × 396 in. Dwight-Lloyd carrying a 6-in. layer of charge. Fuel oil is used to ignite the charge, which is reduced from about 15 per cent to 10 S. Each machine treats about 250 tons per day of a mixture of flue dust, fine ore, and limestone.

The blast furnaces are 50 × 240 in. at the tuyeres and discharge into 18 ft. diameter settlers. The furnace jackets come down only to the top of the crucibles, which are 24 in. deep. The crucibles and settlers are lined with magnesite brick.

The furnace matte is converted in 13 × 30 ft. Peirce-Smith converters, using barren sand and low-grade ore as a flux, to produce white metal and a slag analyzing about 28 per cent SiO_2. The white metal is poured into cast-iron molds, allowed to cool, and then broken up for shipment as already described. The converter slag is returned to the furnace settlers.

Port Colborne Operations.—At Copper Cliff, there are two types of nickel sulphide (white metal) produced for the operations of the Port Colborne refinery: the so-called "regular" sulphide, averaging 69 to 70 per cent Ni, 27 per cent S, and 0.25 per cent Fe; and the "high-copper" sulphide, containing about 72 per cent Ni, 25 per cent S, and 0.4 per cent Fe. Most of the gold and silver in the original ore has followed the copper and has gone with the "tops," but the bulk of the platinum group remains with the nickel in the bottoms.

For the production of nickel oxide for the market, the "regular" sulphide is used. It is ground in ball mills to 0.027 in. and is transferred to lead-lined concrete tanks with filter bottoms. These tanks are partially filled with water, and the crushed matte is sifted in through gratings, which prevents lumping and packing. When the tank is filled, it is first leached with hot water to remove the sodium sulphide. The strong sulphide liquor is sent to storage; the dilute wash waters go to waste.

The washed nickel sulphide is treated with 10 per cent sulphuric acid, which removes about 50 per cent of the iron in the nickel sulphide, *i.e.*, the iron will be reduced from about 0.25 to 0.12 per cent. Some nickel is also dissolved, so that the solution from this step must be treated to recover the dissolved nickel.

The leached oxide is roasted in Edwards furnaces where in the mechanically operated hearth the sulphur is reduced from 27 per cent to less than 4 per cent. The material is mixed at this point with sodium chloride and is roasted at a low temperature in a hand-rabbled hearth. This chloridizes most of the copper and a small amount of nickel. The roasted material is leached in the same way as was done to remove the sodium sulphide, the strong leaches being treated to recover the copper and nickel, the weak washes being used for the first washing of further chloridized sulphide.

The leached chloridized material has a greenish tinge and is known as "green oxide." It contains about 77 per cent Ni, 0.1 per cent Cu, and 0.4 per cent S. It is roasted at about 2300°F. after mixing it with soda ash to remove most of the sulphur. It then is again leached, and after leaching it contains about 77.5 per cent Ni, 0.25 per cent Cu, and 0.005 to 0.008 per cent S, in which condition it is known as black oxide. The nickel and copper in the acid leach of the sulphide and in the chloride leach of the black oxide are recovered by precipitating them with the sodium sulphide from the first hot-water leach. The precipitate is recovered by filter pressing and goes back to the Copper Cliff smeltery.

"High-copper" sulphide for the production of anodes undergoes the same leaching treatment except that it is not ground so fine. After being dried, it is sintered on Dwight-Lloyd machines to give a product containing not over 0.4 per cent S.

Sintering Operation.—In this operation it is necessary to return a large amount of the sintered material, since it has been found that in order to secure a 0.4 per cent S product the feed to the sintering machines cannot be over 6 per cent S. Conse-

quently, enough returns must be used to dilute to this sulphur content. Oil-fired muffles are used to start the ignition, and coke breeze is mixed with the charge to assist combustion. Nickel sulphide (high copper) for the nickel refinery at Clydach, Wales, is partially processed at Port Colborne. It is crushed, ground, and leached, just as in the "regular" sulphide treatment, and then is partially roasted in an Edwards all-mechanical furnace to a sulphur content of 6 to 7 per cent. It is then shipped in barrels to the refinery at Clydach.

The crude oxide or sinter is crushed to ¼-in. mesh and is mixed with crushed low-ash bituminous coal in a drum mixer. This mix is charged into oil-fired reverberatories. The oxide is reduced to metal, melted, and worked to flat pitch, then tapped into anode molds and sent to the electrolytic department.

If pure nickel oxide is being worked with, such as the precipitate from ammonia-carbonate leaching, it is mixed into a paste with flour and made into pellets that are heated in retorts with charcoal for 48 hr. at 1200 to 1300°C., for the production of pure nickel.

Electrolytic Department.—The anodes produced from the crude sinter carry approximately 95 per cent nickel, 2 to 2½ per cent Cu, 0.75 per cent Fe, and 0.75 per cent S. The anodes are cast with lugs for supporting them in the tanks and are about 27 × 36 in., weighing 480 lb. each. Fourteen anodes are placed in a tank.

The electrolytic tanks are constructed of reinforced concrete, mastic-lined, and are built in pairs. The electrolyte contains about 40 g. Ni, 20 g. boric acid, and 35 g. Na_2SO_4 per liter. The cathodes are placed in compartments made of canvas on wooden frames, and the purified electrolyte is fed into the cathode compartment. The anolyte flows out through rubber pipes built into the tanks 9 in. above the bottom, and discharging at the top through spill boxes fitted with wooden weirs.

The electrolyte is kept free from copper by cementation in wooden pachucas on grain nickel. Several of these tanks are used in series. The overflow from the last pachuca tank goes through a Dorr thickener, and any grain nickel carried over goes back to the first pachuca. The solution from the Dorr thickener then goes through a set of tanks into which air is blown, which oxidizes and precipitates the iron as basic sulphate and as hydroxide, along with some nickel. The solution is then filter pressed and returned to the electrolytic circuit. The grain nickel used in the pachucas is produced by reducing nickel oxide with water gas at a temperature below the melting point of nickel.

Starting-sheet Manufacture.—Starting sheets are produced by plating nickel on aluminum or stainless steel blanks. The thin sheets after stripping are fitted with suspension straps or loops cut out of starting sheets and attached by spot welding or clamp punches.

Mond Process.—The coarsely calcined matte from Port Colborne is first roasted to about 1 per cent S, and is then ready for the refining process. In principle, this consists of a reduction to metallic nickel by a mixture of hydrogen and carbon monoxide, the volatilization of the nickel as nickel carbonyl, $Ni(CO)_4$, and the decomposition by heat of nickel carbonyl into nickel and carbon monoxide. In practice, the calcined ore passes through six reducers in series, then through six volatilizers in series, which volatilize about one-third of the nickel as carbonyl. The residual material is mixed with a little fresh material and passed through two more reducers and four volatilizers and then receives a final reduction in one reducer and then passes through three more volatilizers[6].

On the basis of about 5 hr. in each reducer and 16 hr. in each volatilizer, this means about 10½ days for the passage of the ore through the plant.

The reducers are vertical gastight structures, built up of 21 cylindrical cast-iron sections, 6 ft. in diameter, with a central hole 22 in. in diameter. In each

box or section is fitted a horizontal cast-iron plate with a central hole and six supporting lugs, which fix the plate in the middle of the box. A central vertical shaft carries and rotates a series of scrapers on each box and plate. The material falls on the top plate, is pushed to the outer edge by the scrapers, and thence falls to the bottom of the first box. From this position it is pushed to the central hole through which it falls to the next plate, and so on, until it enters an exit conveyer at the bottom.

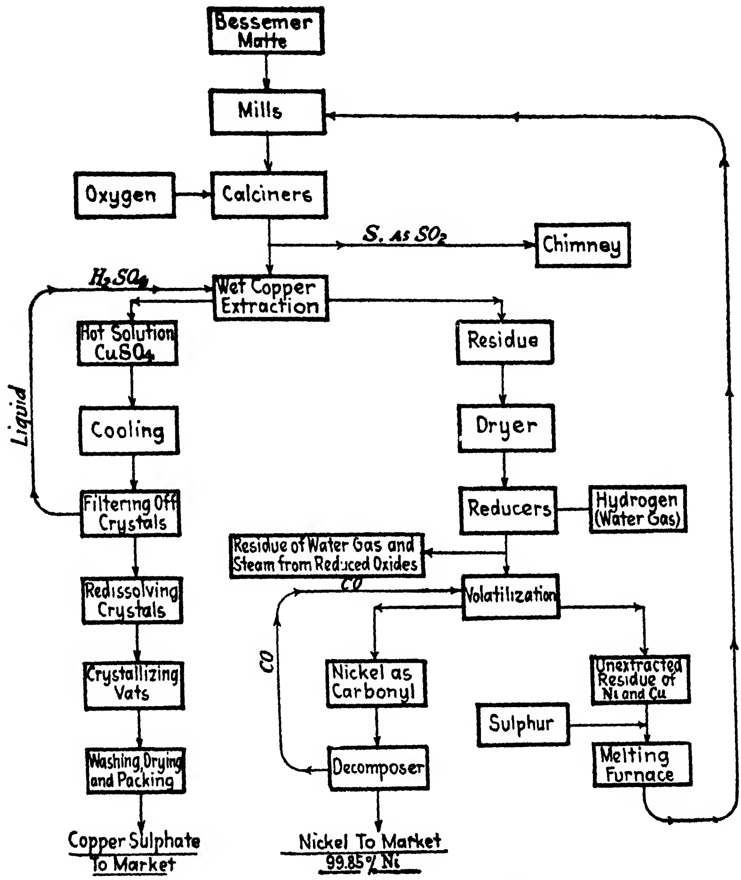

FIG. 2.—Mond-process flow sheet.

A reduction temperature of 350 to 400°C. is maintained by a hot-air circulating system. Theoretically, the reduction is interesting in that it takes place at so low a temperature that the carbon monoxide effects only about 3 per cent of the reduction and the hydrogen about 97 per cent. The reaction with the hydrogen, although endothermic, is, at the temperature employed, twenty to forty times as rapid as is the exothermic reaction with carbon monoxide. The result of this relationship is to give an end gas that is high in CO after condensing the water-vapor out of it and, hence, is admirably suited for use in the volatilizers.

The volatilizers are similar in design to the reducers except that no external heat is necessary. The reaction is exothermic and radiation must be employed to keep the temperature from rising about the optimum of 60°C. The reduced material travels

down through the volatilizers, where it comes in contact with the high CO gases, traveling upward.

Decomposition of Nickel Carbonyl.—In the decomposing apparatus the nickel carbonyl comes into contact with nickel pellets heated to a temperature of about 180°C. The nickel is deposited on the pellets, and carbon monoxide is liberated. Close temperature control is necessary, for above 200°C. the carbon monoxide begins to break down into carbon and carbon dioxide.

The decomposer is made up of a cylindrical cast-iron base in two pieces, carrying six cast-iron decomposer boxes, one above the other. Each box has an external gas ring with burners, and is heated by producer gas. Each decomposer is filled with about 9 tons of nickel pellets before being put in circuit. The bottom box is fitted with a conical piece through which the pellets flow, past an adjustable baffle plate, to a bucket elevator that returns them to the top. The pellets grow as they circulate, and the larger pellets are screened out of the circuit.

The incoming nickel carbonyl gas is supplied to a central vertical tube and passes from this through shielded outlet holes in the middle of each decomposer box. After percolating between the pellets and depositing its nickel, the gas leaves through a water-cooled outlet ring placed between each pair of boxes, is collected in a common vertical main, and is recirculated through the volatilizers in a closed circuit, wastage being made up with carbon monoxide formed by the decomposition of liquid nickel carbonyl supplied by the so-called "medium-pressure plant."

Medium-pressure Plant.—The material discharged from the thirteenth volatilizer (see page 600) is recalcined and fed to the medium-pressure plant. Here it again passes through reducers and is then charged to a number of pressure volatilizers, in which it is subjected to the action of gases containing about 60 per cent carbon monoxide at a pressure of 300 lb. per sq. in. The exit gases from these volatilizers pass through coolers, where the bulk of the nickel carbonyl is condensed as a liquid. The residual gases are expanded to atmospheric temperature, and the residual nickel is recovered in decomposers of the standard type. The liquid nickel carbonyl is then used for the production of make-up carbon monoxide[6].

The Hybinette Process.—This process was employed by the British-American Nickel Corp., at its refinery at Deschenes, Quebec. Bessemer matte of the following composition—Ni, 53; Cu, 28; S, 18; and Fe, 0.25 per cent—was produced at the company's smelter at Nickelton, Ontario. The matte was granulated and shipped to the refinery. The granulated matte was screened through 10 mesh and charged into cementation tanks, through which flowed the foul electrolyte from nickel-plating tanks. Bessemer matte was semimetallic, and the metallic portion cemented the copper; an equivalent amount of nickel went into solution. To facilitate this metal transfer, each tank was equipped with hard-lead steam coils (about 70°F. is necessary). The copper-free electrolyte and the foul solution from plating tanks flowed in opposite directions through a heat interchanger in which a part of the heat in the purified liquor was transferred to the foul liquor before entering the cementation tanks.

The spent matte from the cementation tanks, then containing about 44 per cent Cu and 38 per cent Ni, was excavated and sent to eight-hearth Wedge roasters, and roasted to about 1 per cent S. The hot calcines passed over a screen, the oversize was crushed and returned to roasters, and the fines were discharged into a launder, through which leaching solution conveyed them to leaching tanks of about 90-ton capacity. This leaching solution was depleted electrolyte from the copper-plating tanks (30 g. per l. of Cu and 80 g. per l. of H_2SO_4).

The copper-enriched solution from leaching tanks (Cu, 50 g. per l.; and H_2SO_4, 50 g.) passed through clarifying cones and thence to a series of three-tank cascade electrolytic deposition tanks. These tanks were lead-lined and contained eight cath-

odes and nine lead anodes. The overflow from the third tank of the series returned to roaster launders as leach liquor.

As a certain amount of nickel was dissolved with the copper and accumulated in the copper leach liquor or electrolyte, a portion of the spent electrolyte was continuously removed and passed through a separate series of plating tanks, where the copper was practically all removed. This copper-free solution was evaporated and the nickel crystallized as single nickel salts ($NiSO_4.7H_2O$). Mother liquor, rich in acid, was returned to leaching tanks.

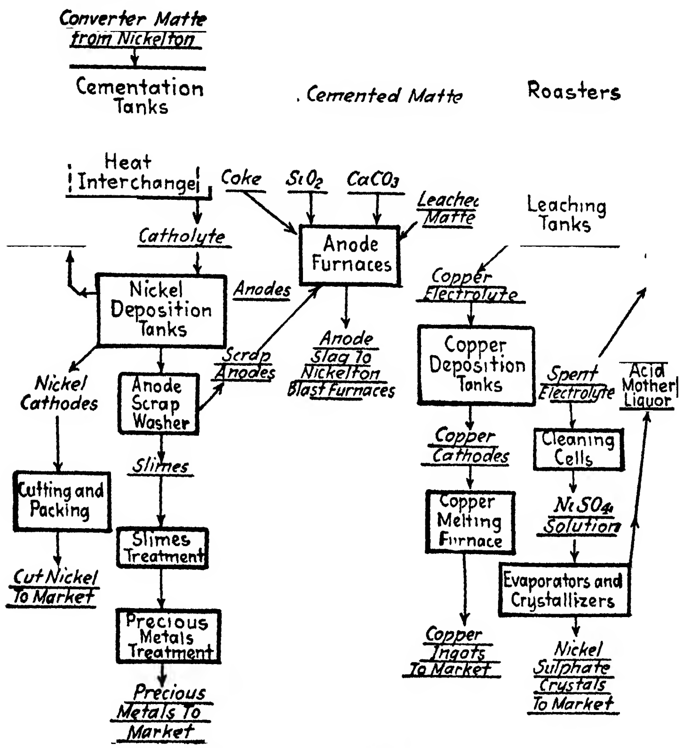

FIG. 3.—British-American Nickel Co.'s flow sheet.

The nickel electrolyte was also continually enriched with nickel in the cementation tanks, where the copper cemented on the matte was replaced by an equivalent amount of nickel. It was necessary, therefore, to withdraw continually portions of the solution, which was evaporated and crystallized as above. The leached, roasted matte was excavated, mixed with coke breeze and limestone, and melted in a three-phase resistance furnace. The metal was tapped intermittently into a brick-lined ladle and poured into cast-iron anode molds (24 × 36 in.). Anodes contained about 65 per cent Ni, 29 per cent Cu, and 0.40 per cent Fe.

The anodes were encased in bags to catch slimes and suspended in lead-lined tanks (36 anodes and 35 cathodes). Cathodes consisted of iron or copper plates (24 × 36 in.) suspended in "Hybinette bags," consisting of wooden frames with canvas sides, acting as diaphragms.

Copper-free nickel electrolyte from cementation tanks (previously described) was fed to cathode bags through rubber tubes from a lead header at a rate sufficient to

maintain a head of about 1 in. over the level in the anode compartment. This was to prevent anolyte containing copper from flowing into the cathode bags and contaminating the nickel. Nickel sheets weighing about 30 lb. were stripped from cathodes about every 10 days, washed with dilute sulphuric acid, and cut into small squares for shipment. Or they were melted in the electric furnace and cast into ingots.

Electrolytic nickel analyzed about Ni, 98.25; Co, 0.75; Cu, 0.03; Fe, 0.50; C, 0.10; and Pb, 0.20 per cent.

Anode scrap was remelted and cast into molds. Slag from the melting furnace was shipped back to the smelter for re-treatment. Slimes from the anode tanks were treated for the recovery of precious metals.

Originally the cathodes were painted with graphite before being placed in the tanks, but a dip in sodium-sulphide solution was found to result in easier stripping and smoother deposits. Frequently, however, patches of nickel were hard to detach, and when the cathodes were replaced in the tanks, trees grew around their edges. If dipped in sodium sulphide, these patches became permanent, or nearly so, and in this case, graphite was used on the cathode surface, being omitted in the nickel patch. The latter usually then came off with the next deposit, when the sodium sulphide dip would again be used.

Nickel starting sheets were experimented with, but in so acid an electrolyte, internal stresses were set up that made the sheets curl when stripped and rendered them useless as starting sheets. While a separate starting-sheet section might have cured this, it seemed an undesirable complication.

Aluminum sheets were also experimented with. The difficulty was in making the plates just rough enough to strip easily without having the deposit flake off in the tank. Light sandblasting at frequent intervals kept the plates in this condition.

NICKEL RECOVERY METHODS ON OXIDIZED ORES

Ore Reserves.—Apart from various deposits of completely oxidized ore where there is little heavy-metal content except the nickel itself, there are immense bodies of lateritic iron ore in various parts of the world, Cuba, Puerto Rico, Gold Coast, Greece, Celebes Islands, Java, and the Philippine Islands. Probably the most important are the Cuban deposits, where some authorities have estimated as high as 3,000,000,000 tons of laterites carrying in the neighborhood of 1 per cent of nickel.

An outstanding feature of the metallurgic experimentation of the last few years has been the attempt to treat these ores for recovery of the contained nickel.

Over 100 different patents have been taken out covering these processes. Space limitations prevent an exhaustive survey, so it is the author's intention to describe only four which are based on radically different procedures. These are ammonia-ammonium-carbonate leaching as exemplified in the Caron process and its development by the Freeport Sulphur Co.; the volatilization of nickel as nickel carbonyl; selective chloridizing; and selective sulphatization.

Freeport Sulphur Process.—This project of the Freeport Sulphur is the most ambitious attack that has ever been made on the problem of treating lateritic ores. The ore is reduced by a mixture of carbon monoxide and hydrogen and then is cooled to the temperature at which nickel carbonyl might be formed in such a concentration of carbon monoxide that nickel carbonyl is not formed in perceptible quantities. The reduction temperature is stated to be about 800 to 850°C.

The ore after cooling is treated with a mixture of ammonia and ammonium carbonate. The ore must be kept from oxygen until after the solvent is in contact with it, but after the solvent is applied, some aeration or oxygenation is necessary in order to cause the nickel and cobalt to dissolve. The nickel apparently goes into solution as $NiCO_3.3NH_3$. After filtration, the solution is heated and basic nickel carbonate is

precipitated. Pawel states (*Mining and Metallurgy*, August, 1943, page 360) that the nickel can also be easily deposited in metallic form by electrolysis of the solution and that if this process is followed there is less likelihood of losing ammonia than there is in driving off the ammonia and then condensing it. The greatest difficulty in the process is this matter of ammonia losses, either through nonrecovery of the ammonia driven off by heat from the solution, or adsorption losses from ammonia clinging to the finely divided iron oxide of the ore. It is possible in laboratory work to separate the cobalt and nickel by careful control of the heat, but it has not been proved that this can be done on the commercial scale.[1] The finely divided nickel oxide absorbs sulphur readily, and if it is dried in contact with combustion gases containing SO_2 or SO_3, an impure product will result.

Nickel Carbonyl Processes.—The Simpson process (U. S. patent 2212459 of Aug. 20, 1940) is based on one of the most extensive sets of experiments ever run on the treatment of nickel ores by the carbonyl process. The ore is reduced and the reduced ore is treated with pure carbon monoxide at 40 and 80°C., which forms $Ni(CO)_4$ mixed with a very small amount of $Fe(CO)_5$. The nickel carbonyl is fractionally distilled from the iron carbonyl, and the temperature is raised, decomposing the nickel carbonyl into nickel and carbon monoxide. This decomposition is usually carried out at about 200°C. The reduction takes place at about 500 to 700°C. using water or producer gas as the reducing agent (U.S. patent 2221061).

This whole process is of course an extension of the classic work done by Dr. Ludwig Mond, on which he based his British patents 12626 of 1890 and 8083 of 1891, his original processes still serving for the refining of nickel at the Clydach Works in Wales.

It may be noted also that the celebrated James Dewar worked on this process, investigating particularly the effect of pressure on the decomposition temperature of nickel carbonyl.

Chlorine Process.—Many inventors have worked with the idea of chloridization, the earliest American patent known to the author having been taken out in 1909 by Adolphe Seigle. The well-known German metallurgist C. A. Brackelsberg took out a selective chloridization patent as early as 1914. Both Charles Hart and E. W. Wescott worked on chlorine volatilization processes. Wescott completely volatilized the iron as ferric chloride, nickel and cobalt chloride being left behind. Hart volatilized only a portion of the iron, which he recovered as Wescott did also, by burning the ferric chloride to ferric oxide and chlorine, leaving a residue greatly enriched in cobalt and nickel (and chromium if present), which he proposed smelting to ferronickel or to 18-8 stainless steel. Unfortunately there is a tendency to form basic chlorides so that the residue is not admirably adapted to blast-furnace smelting.

That selective chloridization has been considered has been spoken of above. A great number of these processes have been patented, of which the best in the author's opinion is the process of E. W. Wescott (U.S. patent 2036664 of Apr. 7, 1936). The ore is treated with a mixture of gaseous hydrochloric acid and water vapor between 180 and 300°C. If the temperature is too low, there is excessive chloridization of the iron, which is also the case if pure hydrochloric acid is used. Under the conditions laid down by the inventor, there is little chloridization of the iron, and what ferric chloride is formed is decomposed by raising the temperature and admitting steam and hydrogen. The nickel and cobalt remain as soluble chlorides and can be leached out.

Selective Sulphatizing.—This idea also has been worked on very considerably. The earliest work known to the author is that of F. A. Eustis and C. P. Perin (U.S. patent 1185187 of May 30, 1916), but the work of C. P. McCormack is probably better known today, though the basic principle of the inventors is the same. In the

[1] It is claimed this has now been demonstrated (June, 1945).

McCormack process (U.S. patent 1575852 of Mar. 9, 1926), lateritic ore is intimately mixed with sodium carbonate or sodium hydroxide and the mixture given a roast under oxidizing conditions. Alumina forms sodium aluminate, and the chromium is oxidized and combines with the soda to form sodium chromate. These are leached out with hot water and the alumina precipitated by means of carbon dioxide. Sodium chromate is crystallized from the mother liquor. The leached residue is then mixed with pyrite and again roasted, the roast gases being recirculated over the roasting ore. At temperatures between 450 and 750°C. the nickel has more of a tendency to sulphatize than has the iron and theoretically, a good separation can be effected of the soluble nickel sulphate from the insoluble iron oxide; however, at least in the author's experiments, the separations are not sharp and the hand labor involved is large. Shortly before the outbreak of the present war the Philippine government made a large-scale test of this process, but apparently did not adopt it, for the treatment of the Surigao ores.

Ralph F. Meyer and Alan Kissock have also done important work on differential sulphatizing.

Direct Smelting Processes.—In some parts of the world are deposits of nickel where there is practically no other heavy metal present. Experiments have been made on these ores, smelting them to produce a calcium-aluminum-silicate slag and a ferronickel with what iron is present, or if necessary, adding a little iron, using the electric furnace for this work. The greatest trouble has been that if any sulphur were present either in the ore or in the reducing agent it was all found in the metal produced.

Before the war the Germans smelted large amounts of ore containing nickel, iron, and chromium for the production of an alloy of iron, chromium, and nickel. The chromium was blown out and eventually recovered from the slag as high-carbon ferrochromium, while the residual nickel iron was used for the production of nickel steel and the like. A discussion of the means by which the chromium content in the ferronickel was held down and a high-chromium slag produced would involve a long excursion into ferrous metallurgy, and hence is omitted here.

The sulphur dioxide leaching of nickel ore was reported to have been experimented with by the Soviet government quite extensively in 1929 to 1931, but it is reported that the experiments did not indicate that the process would be economic on a large scale.

Reduced Nickel.—A special product produced at the Huntington plant of the International Nickel Co. is so-called reduced nickel. Reduced nickel is metallic nickel in a finely granular form, produced by reducing the black oxide of nickel with charcoal at a temperature slightly below 1500°F. It is dull gray and magnetic.

It is of use where a highly soluble form of nickel is desired and where the granular form is acceptable. One of its large uses is in the manufacture of nickel salts. A typical analysis of INCO reduced nickel is as follows: Cu, 0.26; Ni, 97.80; and soluble Ni, 95.80 per cent.

The wet oxide to be reduced is mixed by piling and turning with about 30 per cent of its weight of ground charcoal. The intimate mixture is then charged into an oil-fired roasting furnace with flat rectangular hearth and working doors on each side, which allow hand rabbling of the charge during the reducing process.

The charge in the furnace is leveled off to a depth of about 4 in. The oil burner is then lighted, and heat is gradually applied to the charge. It is rabbled every 30 min. to ensure even heating and to work the charge toward the front end of the furnace. Additional charcoal is added before the final rabble, or after about 3½ hr., and then the charge is drawn into iron drums, covered with charcoal, and sealed.

The drum is allowed to cool for at least 24 hr. The seal is then broken, the material dumped on the floor, screened through ¼-in. mesh wire screen, and put through mag-

netic separators to clean it from charcoal. The separated reduced nickel ready for shipment is rather finely granular. A screen test shows that on an average

90 per cent passes 10 mesh
80 per cent passes 20 mesh
50 per cent passes 50 mesh
20 per cent passes 100 mesh
10 per cent passes 150 mesh

This product is put up in barrels, weighing about 1000 lb. each, and is then ready for shipment.

Properties and Commercial Applications.—Nickel is a silvery-white metal having a strong luster. It is malleable, ductile, somewhat magnetic, harder and stronger than iron, resistant to abrasion, and of high melting point. It is very highly resistant to the action of air, water, nonoxidizing acids, fused alkalies and salts, either fused or in aqueous solution. It is also remarkably resistant to oxidation at high temperatures. It has a magnetic transformation point occurring at about 320°C. in commercial grades.

While nickel is primarily divalent, a few relatively unstable compounds are known in which it is trivalent. A peroxide (NiO_2) is also known. Nickel is, with cobalt and iron, a member of the eighth group of the periodic system. Its atomic weight is 58.68. In normal solutions of its salts, nickel has a solution pressure of about 0.6 volt against the calomel electrode. Its electrochemical equivalent is 0.30425 mg. per coulomb.

Nickel and its compounds exhibit strong catalytic activity in all types of reactions, as illustrated in its commercial use for the hydrogenation of oils.

Metallic nickel gives to its alloys strength, ductility, and resistance to corrosion. With such metals as copper and gold it acts as a powerful decolorizing agent.

Distribution of Nickel.—Nickel is widely used industrially. Arranged roughly in order of their relative importance from the tonnage standpoint, the paths of distribution for nickel are: as nickel steel, Monel metal, nickel-silver and copper-nickel alloys, electroplating, nickel-chromium-iron "heat-resisting" alloys, malleable nickel, coinage, nickel salts for catalysts, etc., and nickel oxide for use in the ceramic industry.

TABLE 1.—COMMERCIAL NON-MALLEABLE GRADES OF NICKEL

Grade	Form	Analyses, per cent						Uses
		Ni-Co	Cu	C	Fe	Si	S	
Electrolytic[1]	24″ × 36″ - 100 lb. plates	99.80	0.04	Tr	15	Nil	Tr	Highest-grade malleable alloys
Shot:								
"X"	Granulated in water	99.15	0.18	12	38	10	0.025	Non-ferrous alloys and crucible nickel steel
"XX"	Granulated in water	99.45	0.08	10	25	05	0.008	
"A"	Granulated in water	98.75	0.18	45	38	22	0.025	Platers' anodes
"F"	Granulated in water	91.75	0.20	30	1.85	5.75	0.025	
Ingot or pig	25-50 lb. pig	99.20	0.30	03	45	03	0.035	Open-hearth or electric furnace steel
Reduced nickel oxide	Powder	98.75	0.15	...	50	....	....	Nickel salts

[1] Electrolytic nickel is malleable, but is seldom used for this property.

Nickel is marketed in various forms, depending on the use to which it is to be put. These are (1) grains, cubes, rondelles, or powder, reduced from the oxide at low temperature without being fused; (2) nickel shot, nickel deposited in concentric layers from nickel carbonyl (gas) without being fused; (3) electrolytic cathode sheets; (4) blocks or shot obtained by reducing nickel oxide at temperatures above the melting point of nickel and casting the resulting metal or pouring it into water, without deoxidation; (5) malleable nickel, produced in the same manner as (4), except that it is treated with a deoxidizer before pouring; (6) nickel salts; (7) nickel oxide.

Most of the commercial production of nickel falls in class (4).

Malleable Nickel.—The properties of malleable nickel at ordinary temperatures are given in Tables 2 and 3 and at elevated temperatures in Table 4.

TABLE 2.—PHYSICAL PROPERTIES OF MALLEABLE (99 PER CENT) NICKEL
(Commercially pure nickel)

Density (specific gravity), 8.85.
Weight per cubic inch, 0.319 lb.
Melting point, 1450°C. (2640°F.).
Shrinkage (pattern), ¼ in. per foot.
Linear coefficient of thermal expansion:
  25 to 100°C., 0.0000130 per degree.
  25 to 300°C., 0.0000145 per degree.
  25 to 600°C., 0.0000155 per degree.
Electrical resistivity, 64 ohms per mil. ft. (10.6 michrom-cm.).
Conductivity about 16 per cent of that of copper.
Coefficient of electrical resistivity, 0.0041 per degree centigrade, or 0.0023 per degree Fahrenheit.
Optical reflection coefficient, 65 per cent.
Thermal conductivity, 0.14 c.g.s. units (about 17 per cent that of copper).
Specific heat (20 to 1400°C.), 0.130 cal. per g.
Latent heat of fusion, 73 cal. per g.
Magnetic induction at 100 gausses field strength, 5000 gausses.
Young's modulus of elasticity, 30,000,000 lb. per sq. in.
Torsional modulus, 1,000,000 lb. per sq. in.
Poisson's ratio, 0.33.

TABLE 3.—MECHANICAL PROPERTIES OF 99 PER CENT NICKEL

Form of material	Tensile properties				Hardness		
	Yield point, pounds per square inch	Tensile strength, pounds per square inch	Elongation in 2 in., per cent	Reduction of area, per cent	Brinell		Scleroscope
					500 kg.	3,000 kg.	
Rods, hot rolled	20,000– 30,000	70,000– 85,000	35–45	50–65	90–110	110–150	15–18
Sheet:							
Annealed	20,000– 27,000	60,000– 75,000	35–45	.....	80–100	....	12–14
Cold rolled, hard	90,000–105,000	90,000–110,000	1–2	.....	130–160	....	30–40
Wire:							
Annealed	15,000– 25,000	60,000– 75,000	20–30				
Hard drawn	110,000–130,000	120,000–140,000	1–2				
Castings	30,000– 40,000	55,000– 70,000	20–30	.....	125–150	....	12–15

Nickel and some of its alloys retain their physical properties to a relatively high degree at elevated temperatures. The data of Table 4 were obtained by the International Nickel Co.

TABLE 4.—PROPERTIES OF 99 PER CENT MALLEABLE NICKEL AND OF SOME OF ITS ALLOYS AT ELEVATED TEMPERATURES

Temperature, degrees Fahrenheit	Rolled "A" nickel	Hot-rolled Monel metal	20 per cent Cupro nickel	Temperature, degrees Fahrenheit	Rolled "A" nickel	Hot-rolled Monel metal	20 per cent Cupro nickel
Tensile strength, 1000 lb. per sq. in.				Yield point, 1000 lb. per sq. in.			
70	81	81	63	70	24	32	
200	82	80	61	200	24	31	
400	84	79	58	400	24	29	
600	83	78	51	600	23	28	
800	83	71	41	800	21	27	
1000	58	51	30	1000	19	23	
1200	45	30	18	1200	17	18	
1400	30	22	6	1400	13	12	
1600	17	15					
1800	11	8					
2000	8	5					
Elongation, per cent in 2 in.				Reduction of area, per cent			
70	51	46	28	70	70	69	
200	51	45	27	200	68	68	
400	52	44	26	400	68	66	
600	51	51	24	600	68	64	
800	50	52	22	800	66	62	
1000	50	29	17	1000	75	31	
1200	48	34	14	1200	76	15	
1400	50	..	23	1400	78	10	
1600	33	..	27	1600	32	15	
1800	36	..	..	1800	40	25	
2000	70	..	..	2000	99	29	

Malleable nickel is the only grade in the production of which deoxidizers are used. Deoxidation is accomplished by the addition of manganese and magnesium in the crucible or ladle before pouring into ingots or castings. The carbon content is adjusted to 0.10 to 0.30 per cent by adding charcoal or nickel oxide and the metal raised to pouring temperature (2800 to 3000°F.). If an electric furnace be used, the deoxidizers should be added in the furnace if possible. Manganese is added first, either as such or as ferromanganese, to the extent to 0.25 to 2.0 per cent. Magnesium is added to the extent of 1.5 oz. per 100 lb. of nickel. It must be held in tongs and plunged below the surface of the molten metal and an excess must be avoided.

The commercial forms of malleable nickel are: hot-rolled and cold-rolled sheets; hot-rolled and cold-drawn rods; cold-rolled strip: seamless and welded tubing; pipe; wire; forgings; castings; and fabricated forms, such as screen, filter, and wire cloth, and wool. The metal may be machined, welded, forged, or brazed.

At least 12 countries use nickel for subsidiary coinage, and it is largely used for household and ornamental stampings and fittings.

For its resistance to corrosion it is used extensively for cooking utensils, dairy and food-handling machinery, laboratory apparatus and equipment for operations, diges-

tions, evaporation, and transport in the manufacture of dyes and intermediates, essential oils, etc. Kettles, stills, fusion pots, especially for cyanide fusions, and other apparatus are made of malleable nickel, castings of which are quite general for heavy equipment of this type. Some nickel is used for valve trim.

For its resistance to oxidation at high temperatures, nickel is used as heat-resisting castings, parts of glassmaking machinery, lehrs and annealing furnaces, burner parts, as wire for spark-plug electrodes, suspension wires of electric-light bulbs, resistance pyrometer tubes, and for combustion boats used in the reduction of tungsten and molybdenum oxides. Nickel wire with high manganese content is practically standard for spark-plug electrodes. The "D" nickel of the International Nickel Co. contains 3 to 6 per cent manganese. It has a specific resistivity of 20 microhms per cc. and a temperature coefficient of 0.0020 per degree centigrade.

Rabble shoes of cast nickel, exposed in Edwards-type roasting furnaces to sulphurizing and oxidizing gases at 600 to 1000°C. and to severe abrasion, outlast cast-iron shoes about four and a half times.

Electroplating.—Substantial quantities of nickel are consumed in such operations, the major portion of which is consumed in the form of platers' anodes which vary in nickel content from 85 to 99 per cent. The chief impurities contained are iron and carbon, which in some cases is added especially to promote rate of corrosion. The modern tendency, however, in these operations is toward the higher purity product. Nickel plating is used for improving in appearance and protecting from corrosion the base metal to which it is applied. Deposits can be effected satisfactorily on iron, brass, copper, zinc, and many of the common alloys.

Relatively only a small amount of nickel is used in nonmetallic combinations. The sulphate and the double-ammonium sulphate are used in nickel plating, while the carbonate, nitrate, and formate are used as sources of reduced nickel for catalysts in chemical processes. The oxide is used sometimes for the under, or holding, coat in enameling steel and for coloring glazes in pottery manufacture. The hydroxide is used in the Edison alkaline storage cell, where it is reversibly altered to nickelic hydroxide during charging and discharging.

Nickel-copper Alloys.—Nickel and copper are mutually soluble in all proportions, giving solid-solution alloys that are malleable both hot and cold. The malleability is obtained by the use of deoxidizers in the same manner as for nickel. Alloys low in nickel have a characteristic pinkish color, which fades progressively until at 25 per cent or more nickel the color is similar to that of pure nickel.

The alloys used commercially range from 2.5 to about 70 per cent of nickel. For special properties, characteristic of the alloys of different nickel content, they are used for driving bands for shells, bullet jackets, condenser tubes, resistance to corrosion and erosion, turbine blading, coinage, valve seats and parts, resistance and pyrometer wire, and remelting purposes. Most of the alloys are known by special names in the industry. More complete information is given in the references cited in the Bibliography at the end of this chapter.

Monel Metal.—Monel metal is the trade-marked name of a nickel-copper alloy which contains approximately 67 per cent Ni, 28 per cent Cu, and 5 per cent of constituents of lesser importance, chiefly iron and manganese. It was originally a natural alloy, there being no separation of the two major constituents nor alteration of their relative proportions in the process of reduction from the ore in which both occur, but it is now corrected to a constant composition. This alloy resembles nickel in color, finish, and properties. It combines, in a single alloy, high mechanical properties with resistance to corrosion, oxidation, and erosion. Its mechanical properties are retained to a large extent at elevated temperatures, as may be seen in Table 4.

This metal may be rolled, drawn, cast, forged, machined, welded, and soldered. It may be had in the form of pig, shot, hot-rolled and cold-rolled sheets, hot-rolled and cold-drawn rods, bars, strip, wire, welded tubing, castings, forgings and fabricated forms, such as wire screen and cloth, filter cloth, bolts and nuts, nails, tacks, rivets, cable, chain, and balls.

The properties of Monel metal are given in Table 5.

TABLE 5.—PHYSICAL PROPERTIES OF MONEL METAL

Density (specific gravity), 8.84.
Weight per cubic inch, 0.319 lb.
Melting point, 1300 to 1350°C. (2370 to 2460°F.).
Shrinkage (pattern), ¼ in. per ft.
Linear coefficient of thermal expansion:
  25 to 100°C., 0.000014 per degree.
  25 to 300°C., 0.000015 per degree.
  25 to 600°C., 0.000016 per degree.
Electrical resistivity, 256 ohms per mil. ft. (42.5 microhm-cm.).
Conductivity about 4 per cent of that of copper.
Coefficient of electrical resistivity, 0.0019 per degree centigrade, or 0.0011 per degree Fahrenheit.
Optical reflection coefficient, 60 per cent.
Thermal conductivity, 0.06 c.g.s. units (about 7 per cent of that of copper).
Specific heat (20 to 1300°C.), 0.127 cal. per g.
Latent heat of fusion, 68 cal. per g.
Magnetic induction at 100 gausses field strength:
  Cast metal, 500 gausses.
  Rolled metal, 1000 to 1500 gausses.
Magnetic transformation point, 93 to 95°C.
Young's modulus of elasticity, 26,000,000 lb. per sq. in.
Torsional modulus, 9,500,000 lb. per sq. in.

Compression tests on hot-rolled rods showed: proportional limit, 35,000 to 40,000 lb. per sq. in.; yield point, 60,000 to 70,000 lb. per sq. in. Resistance to alternating stress in rotating-beam machines, approximately 100,000,000 alternations at proportional limit, *i.e.*, the endurance safe limit. Izod test, 100 ft.-lb. on standard specimen. Charpy test (standard test piece), hot-rolled rod, 100 to 200 ft.-lb. to rupture.

Chemical Properties and Uses.—Monel metal is widely used for its resistance to corrosive conditions. It is used against anhydrous ammonia, either liquid or gaseous; ammonium hydroxide solutions; solutions of or fused caustic alkalies and carbonates; fatty and other organic acids; sea water; solutions of neutral salts; gasoline and mineral oils; phenol and cresols; photographic chemicals, except solutions containing silver, urine, dry mercury, dyeing, and bleaching solutions; alcoholic and other beverages. It is also highly resistant to sulphuric, dilute phosphoric, hydrocyanic, hydrofluoric, acetic, and citric acids, fused cyanides, ferrous sulphate, and dry chlorine. The metal is attacked by solutions that are strongly oxidizing or contain easily reducible compounds and by molten lead and zinc. It is not resistant to hydrochloric, nitric, nitrous, sulphurous, chromic, or concentrated phosphoric acids or to solutions of ferric salts.

It is used for marine propellers, deck hardware, and parts of ships exposed to the action of sea water; pumps, pump liners, rods and valves for sea water, mine waters, and corrosive solutions generally; mining machinery; mine screens; machinery and equipment for dyeing and bleaching; miscellaneous parts of apparatus exposed to corrosive conditions in the chemical and oil industries generally; screen cloth, filter

cloth, roofing, etc. Monel-metal pins and rods in sulphuric acid pickling tanks in the steel industry have exceptionally long life. Large quantities of metal were used in roofing the train sheds of the Pennsylvania Terminal, New York City, the Chicago, Northwestern Terminal, Chicago, and the Central Railroad of New Jersey Terminal, Jersey City, N. J.

For the finish which it may be given as well as for its resistance to corrosion, Monel metal has been largely used for washing machinery, dairy equipment, cooking utensils, hotel, hospital and restaurant equipment, apparatus for the manufacture of food products, knives, golf heads, small fittings, trim, and stampings.

Monel metal is resistant to erosion and retains much of its strength at high temperatures. It is used for these properties for turbine blading, gas-engine valves, seats and spindles in pressure valves, plugs in oil stills, etc. It will resist oxidation satisfactorily at temperatures up to 800°C., but should not in general be used at higher temperatures. Monel metal is used to some extent as resistance wire and as spark-plug electrodes.

Copper-nickel-zinc Alloys.—These alloys are known collectively as German silver or nickel silver. They are used in a wide variety of compositions and under various trade names for cutlery and table flatware, keys, jewelers' wire, brazing solder, watchcases, etc. For some uses, small amounts of lead or iron are added, but the general range of compositions falls within the limits Ni, 5 to 30; Cu, 45 to 75; and Zn, 5 to 30 per cent. The alloys are white to slightly yellowish in color, malleable hot or cold, easily worked, and obtainable in the usual brass-mill shapes. They are also used in the form of sand castings. Manufacturer's recommendations should be sought for the correct alloy for any specific purpose.

These alloys take an agreeable finish, and many are resistant to corrosion. Consequently, considerable quantities are used for ornamental castings and stampings, plumbing fixtures, and parts of food-handling apparatus. Some metal, in the form of wire, is used as a high-resistance metal in electrical work.

Nickel-chromium Alloys.—Nickel-chromium and nickel-chromium-iron alloys are very highly resistant to oxidation at high temperatures and to chemical corrosion, particularly under oxidizing conditions. They are malleable and are used both in the wrought form for wire, etc., and almost entirely in the cast form for annealing boxes, carbonizing boxes, furnace parts, enameling racks, etc. These alloys have high electrical resistivity with low-temperature coefficients and are used in large quantities, as wire or ribbon, for heating elements in electrical apparatus and for other electrical properties. They are marketed under various trade names and range in composition as follows: Cr, 5 to 20 per cent; Fe, 5 to 40 per cent; Ni, balance.

Nickel Steels and Nickel-iron Alloys.—Nickel and nickel-chromium are the most widely used of alloy steels. Ordinary nickelsteel containing about 3½ per cent nickel is used for automobile parts, bridge and structural steel, die blocks, locomotive forgings and castings, machine and machine-tool parts, ordnance, and power-plant equipment. These steels are used mainly in the heat-treated condition, in which form nickel refines the pearlite grain and increases hardness, yield point, and tensile strength without notably reducing ductility. Fatigue resistance and endurance under alternating stresses are increased and segregation is lessened. The addition of chromium to nickel steels increases the beneficial effects of nickel, and such steels are used to as great or greater extent than straight nickel steels as heat-treated forgings for automobiles and other construction. Molybdenum-nickel steels are also in general use.

Nickel steel of low carbon content (0.1 to 0.2 per cent) is superior to carbon steel for casehardening both in uniformity of case and in mechanical properties of core after heat-treatment.

The compositions of the most widely used nickel steels falls within the limit: Ni, 3.25 to 3.75; Mn, 0.5 to 0.8; and C, 0.1 to 0.5 per cent Five per cent nickel steel is used for casehardened parts to withstand particularly severe service conditions.

Nickel-chromium steels are described as low, medium, and high, and they range in composition as follows: Ni, 1.0 to 3.75; Cr, 0.45 to 1.75; and Mn, 0.30 to 0.80 per cent. The high nickel-chromium steels are used where particularly high physical properties are desired in all carbon ranges.

Nickel-iron alloys relatively high in nickel exhibit remarkable magnetic properties and wide variation in their thermal expansivity in normal temperature ranges. Many are also resistant to corrosion. Invar, 36 per cent nickel, has an extremely small coefficient of expansion at ordinary temperature and is used for measuring tapes, parts of precision instruments, etc.

Nickel and nickel-chromium cast iron is being used commercially today for rolling-mill parts such as rolls, mill guides, pipe-bending dies, pipe balls, etc., for automobile engines and other cylinder castings, for pistons and piston rings, for cast-iron cams, for sheet and plate metal forming dies, in various thin section castings, prominently resistance grids—the amounts used varying from as little as 0.10 per cent (but usually not less than about 0.40 per cent) up to 5.0 per cent nickel and from 0 to 0.50 per cent chromium.

The principal useful effects of nickel and suitable nickel-chromium combinations in gray iron have proved to be the following: (1) to increase strength from 10 to 50 per cent, requiring 0.50 to 1.0 per cent nickel together with 0 to 0.50 per cent chromium depending on the grade of iron, a higher silicon iron requiring a greater addition of chromium; (2) to increase hardness 20 to 50 points Brinell without impairing machinability, requiring similar amounts of alloy; or raising the hardness 100 points Brinell, with the iron still remaining machinable, but less readily so, with larger amounts of alloy; (3) to reduce edge, surface, and corner chilling on thin sections or eliminate hard spots in castings made with comparatively hard iron and thus improve machinability, requiring 0.50 to 5 per cent nickel depending on conditions; (4) to increase toughness and deflection particularly of thin section castings by eliminating chill and hard spots, requiring also 0.50 to 5 per cent nickel; (5) to refine grain and produce denser, less open castings requiring from 0.15 to 1.0 per cent nickel together with small amounts of chromium if desirable; (6) to equalize hardness and strength and machinability over large sections or between small irregular sections.

Cast iron is itself a most complex and variable material, and the use of these alloys in conjunction with it requires careful adjustment of the amount of the additions to the grade and composition of iron used as well as to the type and section of casting in question. Disappointing results may be obtained when alloy additions are made that are not suited to the particular conditions, and some tests have been made also on cast iron of high alloy content—up to 30 per cent nickel—and consideration is invited to their interesting and unusual properties as suited to special applications.

Miscellaneous Alloys.—Illium, a complex alloy of Ni and Cr with lesser amounts of Cu, Mo, W, Mg, Fe, Al, and Si, is very highly resistant to corrosion. It is practically unattacked in 25 per cent nitric acid solution.

Nickel-manganese, nickel-copper-manganese, and nickel-aluminum alloys are used in the form of resistance wires and as parts of pyrometer thermocouples.

Nickel has been added in small amounts to many other alloys of industrial importance, in which it acts chiefly to increase hardness without decreasing ductility. Light aluminum alloys, aluminum bronzes, and some brasses and bearing metals are to be noted in this connection.

Nickel alloys have been used as substitutes for platinum ware, and so-called white gold is an alloy of nickel and gold.

A high-silicon nickel alloy in the form of shot and containing up to 5 per cent silicon is used for tumbling and burnishing purposes. It is harder than iron and does not rust.

Alnico, the remarkable magnet material, contains Al, 10; Ni, 18: Co 12; Cu, 6; Fe, 54 (C. W. Drury, *Mineral Ind.*, 1938, p. 114).

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CHAPTER XXII

TUNGSTEN, VANADIUM, URANIUM, AND MOLYBDENUM

H. A. Doerner[1]

Introduction.—Among the elements usually thought of as rare, vanadium, uranium, tungsten, and molybdenum stand out because of their importance in ferroalloys. These are, therefore, treated at length in this section. It is, however, also necessary to consider uranium as the mother of radium, and to treat it in that connection, which is done in the succeeding chapter.

VANADIUM

(Atomic weight = 51.0)

Occurrence.—Vanadium is never found free in nature. Its ores are fairly widely distributed, but seldom occur in quantity in any one locality. The principal ores are patronite, roscoelite, carnotite, vanadinite, cuprodescloizite, zinc descloizite, mottramite, and pucherite. Small concentrations of vanadium have been found in certain iron ores, in phosphate rocks, and in carbonaceous materials such as oil, oil shale, and coal. Flue dust from the combustion of Venezuelan oil contains 20 to 40 per cent V_2O_5. Vanadium is now being recovered as a by-product from these low-grade sources, because a constantly increasing demand is depleting the important ore deposits.

Patronite is an impure vanadium sulphide found in Minasragra, Peru. The composition is approximately V_2S_9, and it is associated to a certain extent with carbonaceous material, pyrites, and free sulphur. The area in which the ore lies[2] is along the western limit of a broad anticline in Jura-Trias and Cretaceous rocks. A section shows the series in this locality to be composed of green shales, thin beds of limestone, and red shales. Vanadium is found only in the red shales. The deposit proper appears to be a lens-shaped mass, 28 ft. wide and 250 ft. long. The mineral that constitutes the larger portion of the deposit has been called "quisqueite." It is a black carbonaceous substance containing sulphur, with a hardness of 2.5 and a specific gravity of 1.75. There is also a lesser quantity of a cokelike material with a hardness of 4.5 and a specific gravity of 2.2. Neither of these contains vanadium. The vanadium is mostly in the southern end of the ore body, and to a depth of 20 ft. is largely in the form of a red calcium vanadate, and carries as much as 50 per cent vanadic oxide. It occurs in pockets and fills the cracks and fissures in a fine shale.

Below this shale is the mother lode. It is 9 to 30 ft. thick and extends along the greater length of the deposit. It carries as high as 10 per cent vanadic oxide and nearly as much sulphur. On the east and south sides below the mother lode is found a hard blue-black vanadium shale carrying as much as 13 per cent vanadic oxide and 4 to 5 per cent sulphur. Patronite, the main vanadium mineral, is greenish-black and has a hardness of 2.5 and a specific gravity of 2.71. It contains 19 to 24.8 per

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[2] Hewett, D. F., *Eng. Mining Jour.*, Vol. 82, p. 385, Sept. 1, 1906; Hillebrand, W. F., *J. Am. Chem. Soc.*, Vol. 29, p. 1019, 1907.

cent vanadic oxide and sometimes 50 per cent of combined sulphur. This deposit in Peru constitutes the largest known source of vanadium at the present time and furnishes the Vanadium Corp. of America with its major supply of ore. As this company has been the largest producer of ferrovanadium and vanadium compounds in the world, patronite is by far the most important ore of vanadium from the commercial standpoint.

Roscoelite, or vanadium mica, is the second most important vanadium mineral commercially. It has a somewhat indefinite composition, the formula $H_8K_2(MgFe)(AlV)_4(SiO_3)_{12}$ representing its composition fairly well. It exists in minute scales of a brown to greenish-brown color. Sometimes the color is actually green. The specific gravity is 2.92 to 2.94. It is found in many localities, but the extensive deposits in San Miguel and Montrose counties, Colorado, are the only ones that have been exploited extensively.

Carnotite is mainly of importance on account of its uranium and radium content, but also carries usually 3 to 5 per cent V_2O_5 in ordinary commercial ores. It is found mainly in southwestern Colorado and eastern Utah, but also exists in smaller quantities in other localities, such as South Australia and Portugal. It is a potassium uranyl vanadate of the following approximate composition: $K_2O.2UO_3.V_2O_5.3H_2O$. The crystals are canary yellow in color and usually exist as incrustations on other minerals, or are disseminated through a sandstone in which they are usually found. It also contains small traces of calcium and barium. Other deposits of vanadiferous sandstone similar to roscoelite or carnotite have been more recently discovered in Colorado and Utah; of these one near Rifle in Garfield County, Colorado, appears capable of considerable production. Another is reported in Emery County, Utah.

Vanadinite, or lead vanadate, is widely distributed, especially in certain of the western states of the United States, particularly Arizona, New Mexico, Nevada, and California. The largest deposits are in Arizona, where it is frequently associated with wulfenite, or lead molybdate. The deposits are almost always low grade, and for this reason this mineral has not been used to any great extent as a source of vanadium in the United States. In Mexico, the vanadinite occurs at Villarosales, Chihuahua. In Spain, important deposits of vanadinite occur near Santa Marta, Estramadura. The ore is found in a sandstone that contains on an average 3 per cent vanadic oxide. This can be concentrated, and these deposits supplied most of the vanadium used in the world up to the opening of the Peruvian mines. The mineral occurs in prismatic hexagonal crystals, and has a specific gravity of 6.6 to 7.11. It varies in color from ruby red to yellowish and even brown.

Cuprodescloizite is a hydrated lead-copper vanadate of the probable composition $(PbCu)_2(OH)VO_4$. Commercial samples of the ore may carry as much as 23 per cent PbO, 7 per cent CuO, and 8 to 10 per cent V_2O_5. The largest deposit of this mineral known at the present time is in the Shattuck mine at Bisbee, Ariz., although it is found in a few other localities in the United States.

Zinc descloizite is a mineral very similar to cuprodescloizite, where the zinc replaces the copper. It is found in Nevada, especially around Goodsprings, in New Mexico, in Arizona, and in Argentina. There has been a considerable production of vanadium from descloizite obtained as a by-product in the treatment of zinc ores at Broken Hill, Rhodesia. Mottramite, a vanadate of lead and copper, and pucherite, a bismuth vanadate, are of lesser importance than the minerals already described. Mottramite has been produced and shipped from Tsumeb, Southwest Africa.

Extraction from the Ores.—The method of extraction that can be used for vanadium ores varies materially with the ore and its grade. In general, a different metallurgical process must be used for every mineral treated, although there are, of course, some general similarities between the methods used.

Patronite is treated by first roasting in order to eliminate the sulphur as far as possible. It can then be leached with sulphuric acid, filtered, and the filtrate evaporated to a crude vanadic oxide, or the roasted ore can be leached with alkali, sodium carbonate or caustic soda, which will dissolve the vanadium as sodium vanadate. From this a high-grade vanadic oxide can be obtained by acidifying with sulphuric acid. More recently, the roasted concentrate is reduced directly to ferrovanadium in an electric furnace.

Roscoelite has been treated for many years in plants at Newmire, Rifle, and Urvan, Colorado. The crushed ore, mixed with salt and often a small amount of pyrites, is roasted to convert the vanadium to a water-soluble vanadate. After the latter is extracted by leaching with hot water, vanadic acid is precipitated by boiling the acidified solution. This precipitate is separated by filtration, dried, and then fused to remove combined water. A high-grade product containing 88 per cent V_2O_5 thus obtained is usually converted to ferrovanadium by reduction in an electric furnace.

At first, carnotite was treated primarily for its radium content, and vanadium was considered a by-product. Since the advent of low-cost radium from the Belgian Congo and northern Canada, these ores are primarily a source of vanadium, whereas radium and uranium are now only by-products. Early methods that do not obtain a high recovery of vanadium have been abandoned or modified.[1]

Metallurgical methods for the treatment of carnotite are discussed more fully in the chapter on radium. They may be classified by their initial operation as (1) acid leach; (2) digestion, and extraction with sodium carbonate solution (usually with some free caustic); (3) bisulphate (niter cake) fusion; (4) other sintering or fusion treatments. Of the acid methods, sulphuric gives the best extraction of vanadium, hydrochloric is also good, but nitric acid is very inefficient and requires a subsequent alkaline leach. Sodium carbonate solution also gives a poor extraction of vanadium even at autoclave temperatures. Fusion with niter cake, followed by a water leach, extracts the vanadium completely. Alkaline fusions may also give high recoveries, but are unsatisfactory because of furnace-lining and filtration difficulties.

From a soda solution, uranium is precipitated by sodium hydroxide after neutralizing the carbonate. The vanadium is obtained by neutralizing the filtrate from the uranium and either adding a slight excess (0.05N) of sulphuric acid and boiling to precipitate vanadic acid, or adding a metal salt (ferrous sulphate, calcium chloride) to form the corresponding vanadate. From an acid leach, vanadium is precipitated with uranium and a portion of the basic elements present by carefully neutralizing and boiling. When sulphuric acid is present in large excess, it is economical to neutralize most of it with lime or limestone and filter off the calcium sulphate before precipitating the vanadium. In some cases the vandium precipitate is reduced to ferroalloy, but usually additional refining is necessary. This may be accomplished by extracting the precipitate with hot soda solution and precipitating as previously described for alkaline solutions.

Vanadinite was originally treated by leaching with sulphuric acid. This dissolved the vanadium and left the lead as insoluble lead sulphate, from which the lead could be recovered by smelting. The process was not a success, because the action stopped after a short time, owing to the crystals of the vanadinite being coated with the lead sulphate, which prevented further action. J. E. Conley has thoroughly studied the treatment of vanadinite.[2] The method recommended by him is to fuse the vanadinite concentrate with a mixture of soda ash and caustic soda, which gives a better melt and a better recovery than soda ash alone. The lead is recovered as metallic lead,

[1] DOERNER, Process for Extracting Radium from Carnotite, *U.S. Bur. Mines Repts. Investigations* 3057, December, 1930.

[2] *Chem. Met. Eng.*, Vol. 20, No. 10, p. 514.

and the vanadium is precipitated by means of slaked lime, giving calcium vanadate as a product. If any trace of molybdenum is present, the latter metal does not come down with the vanadium and is thus eliminated. The calcium vanadate can be treated with sulphuric acid, the precipitated calcium sulphate filtered off, and the vanadium recovered as high-grade vanadic oxide.

Cuprodescloizite has never been treated commercially, but, as it constitutes an important and potentially fairly large source of vanadium, Conley's method is of interest.[1] The object is to recover the lead, copper, and vanadium. Conley found that a sulphuric acid leach gives a fairly satisfactory extraction, but his preferable method is to subject the ore to a preliminary fusion with niter cake, followed by a hot-water leach, and then treat the residue with sulphuric acid. By heating the ore with an equal weight of niter cake, approximately two-thirds of the ore can be decomposed and the corresponding values extracted. The remaining values are then extracted by leaching the residue with about one-half as much acid as is required in a straight acid treatment.

Zinc descloizite up to the present time has not been treated commercially. The principal deposits in Nevada carry considerable quantities of calcite, which make an acid treatment expensive and, therefore, undesirable. Doerner[2] has shown that a more economical method is the fusion of zinc descloizite concentrate with carbon, caustic soda, and soda ash to convert the vanadium to water-soluble sodium vanadate and separate the lead and precious metals as bullion. The vanadium is leached from the slag, acidified with sulphuric acid, and precipitated as vanadic acid by boiling with steam.

Most vanadium ores are not readily amenable to concentration. Patronite is partially concentrated by roasting. Roscoelite was never concentrated at Newmire, Colo., the ore being treated direct. The writer, however, knows of one gold ore in California containing roscoelite from which a high-grade vanadium concentrate has been obtained during the concentration of the ore for gold. Carnotite has been concentrated by both sliming and dry concentration, *i.e.*, attrition and dusting. Preliminary roasting increases the extraction, especially with carbonaceous ores. Vanadinite is easily concentrated by the usual methods involving tables and slimers. It is, however, difficult to separate vanadinite from wulfenite, a mineral with which it is frequently associated, owing to the fact that both minerals have almost the same specific gravity. Cuprodescloizite and zinc descloizite will also concentrate on tables and slimers, but no commercial plants are known to the writer. The main difficulty is a high loss in the slimes.

Metallic Vanadium.—Metallic vanadium has been produced by Gin[3] by the electrolysis of a solution of vanadium trioxide in fused calcium vanadate. The material may also be prepared by the aluminothermic method, and by reducing the dichloride in hydrogen, in which case the metal is a light whitish-gray powder. The metal has a hardness greater than that of steel or quartz. It takes a good polish and is not affected by air. If the powdered metal is thrown into a flame, or rapidly heated in oxygen, it burns brilliantly. Its specific gravity at 15° is 5.5.

Ferrovanadium.—As the principal use of vanadium is in steel and as the vanadium is added to the steel in the form of ferrovanadium, the manufacture of this product is of great importance. Formerly, 75 per cent of the ferrovanadium produced in this country was made in the openhearth or crucible furnace by a modification of the Thermit process, using aluminum as a reducing agent.[4] The remainder was produced

[1] *Chem. Met. Eng.*, Vol. 20, No. 9, p. 465.
[2] *U. S. Bur. Mines Repts. Investigations* 2433.
[3] *Electrochem. Met. Ind.*, 1909, No. 7, p. 264.
[4] *Bull. A.I.M.E.*, August, 1919, p. 1342.

by the electric furnace, using 90 per cent silicon as the reducing agent. Recently, the difficulties of reduction with carbon in the electric furnace have been surmounted,[1] thus eliminating expensive reducing agents.

A satisfactory ferrovanadium for commercial purposes contains 30 to 40 per cent vanadium and not more than 0.5 per cent C, 1 per cent Si, 2 per cent Al, 0.1 per cent S, and 0.1 per cent P. It has a good fracture, is not crystalline, and is bright gray in color. Too much carbon is injurious, because it makes a carbide with the vanadium, which is not satisfactory in steel making. In the aluminothermic or Goldschmidt method, vanadium oxide or iron vanadate is reduced with aluminum shot in a gas-fired openhearth furnace, slagging off the alumina by the addition of soda ash or fluor spar. When the oxide is used, iron turnings must also be added. The process is exothermic, but it is sometimes necessary to apply external heat in order to maintain the temperature required for a fluid melt. This may also be accomplished by adding oxidizing agents, such as niter, intimate mixing, and rapid rate of feed, with large scale of operation. The use of iron vanadate requires more aluminum than the oxide. When applied to complex ores, this method presents great difficulties, as the charge must be calculated so as to eliminate all undesirable elements in the slag and at the same time produce a good recovery of high-grade alloy and the proper amount of heat.

Silicon or ferrosilicon gives a satisfactory reduction in the electric furnace. The raw materials required are steel turnings, vanadium oxide, silicon, lime, and fluor spar. If iron vanadate is used, the steel turnings are not added. All material should be low in phosphorus, but sulphur can be eliminated with the slag by remelting.

In the method developed by Saklatwalla for electric-furnace reduction with carbon, the ore-flux mixture is fed continuously into a localized zone of extremely high temperature, which is obtained by high voltage and current density, combined with close spacing of the electrodes. In this way the vanadium is supposed to be reduced directly from the pentavalent form to the metal, without the intermediate formation of the infusible and insoluble lower oxides that caused trouble in previous attempts. The furnace is three-phase, rectangular, with water-cooled bushings for three 12-in. graphite electrodes. It is automatically charged through water-cooled bushings in the cover.

The melting point of ferrovanadium, practically free from other elements and containing 40 per cent vanadium, is about 1480°C. The melting point becomes gradually lower as the amount of vanadium is decreased until 35 per cent is reached, when it melts at 1425°C., and remains stationary until the alloy contains 30 per cent. At this point the melting point gradually rises to about 1450°C.

Uses of Vanadium.—The chief use of vanadium is for making vanadium steel. The general effect of this rare element on steel is to increase the elastic limit and tensile strength without reducing the ductility. It is usually alloyed with chromium or manganese to give chromium-vanadium or manganese-vanadium steel, and is also used in openhearth and high-speed tool steels. Vanadium is found in much of the steel used in motor cars, locomotive axles, rock drills, etc. The metal causes oxides and nitrides present to pass into the slag, and a certain portion of it also goes into solid solution, rendering the metal more coherent and less liable to disintegration. The quantity of vanadium added to steel is small, the amount usually being between 0.1 and 0.4 per cent.

Other uses for vanadium are as alloys with copper and aluminum. These alloys make excellent castings. It has been used in photography for toning silver bromide plates to a green color. Vanadium salts have also been used in pottery and glass, and as mordants.

[1] SAKLATWALLA, *Jour. Ind. Eng. Chem.*, Vol. 14, No. 10, p. 968.

The chemical activity of vanadium and the large variety of its compounds will probably lead to a much wider chemical use. Vanadium pentoxide is used as a catalyst in the synthesis of ammonia and also in the oxidation of sulphur dioxide. The catalyst is prepared by heating briquettes made of 10 parts alumina and 1 part ammonium vanadate.[1]

Analytical Methods for Vanadium.—Vanadium in an ore can be recognized qualitatively in the following manner: The ore is ground and boiled with hydrochloric acid, filtered, and to the cold acid solution hydrogen peroxide is added. A deep-red color indicates the presence of vanadium. In a mineral such as roscoelite, which is with difficulty soluble in hydrochloric acid, the ore should be fused with sodium carbonate, leached with water, filtered, and the filtrate made acid with hydrochloric acid. On adding hydrogen peroxide, the red color will then be obtained. The choice of a quantitative method will depend on the ore, or vanadium compound, to be analyzed. Full analytical details are given in *U. S. Bureau of Mines Bulletins* 70 and 212. The following method is quick and applicable to a large variety of vanadium ores, especially those which contain little insoluble material and are decomposed by acids. Weigh out a 1-g. sample of the pulverized ore, and add 25 cc. of concentrated hydrochloric acid. Heat on a hot plate to a small volume, then add 10 cc. of concentrated nitric acid and continue heating until decomposition is complete. Remove from the hot plate, cool, and dilute to about 25 cc. Now add 10 cc. of concentrated sulphuric acid, and heat to copious fumes.

Cool slightly and carefully add about half a gram of potassium permanganate. Again heat and cool, then add 5 cc. of water and 10 cc. of hydrochloric acid and evaporate to copious fumes of sulphur trioxide. Repeat with two more evaporations of 5 cc. of hydrochloric acid. Cool and dilute to about 150 cc., warm to dissolve the ferric sulphate, and then titrate at 70 to 80° with $0.05N$ $KMnO_4$ to a pink which persists for half a minute. It is advisable to run a blank determination, which usually requires 0.4 to 0.5 cc. of $0.05N$ $KMnO_4$. Fe factor $\times$ 1.63 = V_2O_5. In an insoluble mineral, such as roscoelite, it is advisable to filter off the insoluble material and to treat with hydrofluoric and sulphuric acids in the usual manner to eliminate the silica, and then to redissolve in a mixture of hydrochloric and nitric acids. The method is applicable in the presence of large amounts of iron; molybdenum does not interfere; and arsenic, if present only in small amount, may be overlooked. Large amounts of arsenic, however, should be removed by first passing sulphur dioxide through the solution after evaporating the first time to sulphur trioxide fumes, boiling off excess, and passing in hydrogen sulphide. Chromium interferes, but is seldom met in vanadium ores.

URANIUM

(Atomic weight = 238.2)

Occurrence.—The principal ores carrying uranium are pitchblende, carnotite, autunite, and torbernite. Pitchblende is an impure uranium oxide with rare earths, carrying traces of lead, calcium, iron, bismuth, manganese, copper, silica, and aluminum. The specific gravity varies from 6.4 to 9.7, and the hardness is usually about 5.5. Carnotite is described under Vanadium. Autunite is hydrated uranium-calcium phosphate, with the formula $Ca(UO_2)_2(PO_4)_2.8H_2O$. It is a bright-yellow mineral, usually crystallizing in orthorhombic plates, and has a specific gravity of 3.5 to 3.9. Torbernite is a copper-uranium phosphate with the formula $Cu(UO_2)_2$-$P_2O_8.8H_2O$. The crystals are tetragonal with a pearly luster and of an emerald-green

[1] U. S. patents 1420201 to 1420203.

color. The specific gravity is 3.4 to 3.6. A further description of uranium minerals and their distribution can be found in the chapter on radium.

Extraction from the Ores.—All uranium minerals carry radium. The amount of radium is usually proportional to the amount of uranium present, although this is not always the case. In primary minerals the equilibrium amount of radium is present, but in secondary minerals, such as autunite and torbernite, the proportion of radium to uranium varies and is often as low as 60 or even 50 per cent of the equilibrium amount. Notwithstanding this fact, uranium minerals are now always treated for their radium content and not for the uranium, the recovery of the latter being of secondary importance. Consequently, the metallurgy of uranium is really the metallurgy of radium, and full details concerning the treatment of uranium ores will be found in the chapter on radium. In order to obtain the uranium alone, practically the same methods that are used for the extraction of radium can be used, the only difference lying in the fact that the radium need not be precipitated as a radium-barium sulphate, this step being omitted. Any method that gives a good extraction of the radium may be used to recover uranium, as it is necessary, of course, to decompose the mineral thoroughly in order to get the radium.

Uranium is usually recovered as sodium uranate, carrying considerable vanadium. The oxide (UO_2) may be prepared from this by the Parsons method, which consists of fusing the sodium uranate with salt and a little carbon. The fused product is leached and washed, everything going into solution except the UO_2.

For analytical purposes, uranium can be extracted from one of its ores by fusing with an excess of sodium carbonate. The melt is broken up, boiled with water, and filtered. The uranium goes into solution as the double carbonate of sodium and uranium, and will contain only small traces of aluminum and iron. On the addition of caustic soda in excess, followed by boiling, the uranium is precipitated as sodium uranate. If an ore is treated which also carries vanadium, the latter element will also be found in solution with the uranium. On the addition of sodium hydroxide, the uranium is precipitated, as already stated, and the vanadium remains in the filtrate. It is practically impossible, however, in such a case to precipitate the uranium free from vanadium. Commercially, the precipitate nearly always carries 5 to 8 per cent V_2O_5. The formula of sodium uranate is $Na_2U_2O_7$, and it usually possesses 6 molecules of water of crystallization.

Concentration Methods.—Most uranium minerals can be concentrated mechanically. This is largely due to the fact that the specific gravity of these minerals is high, particularly pitchblende. Pitchblende can be concentrated by the use of jigs, tables, and slimers. On the table it appears as a black streak representing the heaviest mineral present. Next to this is pyrite, and usually a portion of the pitchblende is found in the pyrite, which constitutes a middling that must either be reground and re-treated, or handled chemically. As the crystals of carnotite are extremely small, this mineral is not amenable to ordinary concentration methods. It can, however, be concentrated in two ways: (1) by dry methods, and (2) by sliming. The most satisfactory dry method involves the use of the ordinary Raymond pulverizing machine with a tubular dust collector. This has a beater chamber containing two sets of rapidly revolving beaters. Over the chamber is a cone of galvanized iron, within which is an inner cone, provided at its lower end with a swinging discharge gate. The two cones are connected at their upper ends by a number of small gate shutters and have a common top or cover plate. A large pipe from the center of the top leads to an exhaust fan, mounted on the same shaft as the beaters. This fan discharges into a cyclone dust and air separator, which is connected by a return pipe with the beater chamber of the pulverizer. A small pipe leads from this return pipe to a tubular dust collector. The Raymond mill is used extensively to pulverize

cement, paints, etc. In the sliming method the ore is ground and then stirred in water, getting as much attrition as possible in order to remove the carnotite crystals from the silica grains. The latter settle quickly, and the carnotite with other fine material is slimed off into another vat and allowed to settle. Undoubtedly, torbernite and autunite could be concentrated in the same way as carnotite, but up to the present this has not been commercially carried out.

Metallic Uranium.—Metallic uranium was first prepared in the electric furnace by Moissan.[1] He used 300 parts of U_3O_8 and 40 parts of sugar charcoal and reduced the mixture in a carbon tube in the electric furnace. The crude product contained carbon and was purified by heating in a crucible, brasqued with U_3O_8. This crucible was embedded in another brasqued with titanium, the object being to prevent action of nitrogen on the reduced uranium. The metal may also be prepared by the electrolysis of the fused double chloride of uranium and sodium in an inert atmosphere, using carbon electrodes.[2] Keeney[3] has prepared the metal by reducing U_3O_8 with carbon in a Siemens furnace with magnesite walls and carbon bottom. The metal was allowed to cool in the furnace. He got a product containing 88 per cent U, 3.67 per cent C, and 2.47 per cent Si, which really consisted of uranium metal and uranium carbide.

Ferrouranium.—Many unsuccessful attempts were made to produce ferrouranium before success was finally achieved. The main difficulty met with was that a low-carbon alloy could not be made by variation of the carbon in the charge, because there was such a low recovery of uranium, both when the amount of carbon charged was about the theoretical amount required, and when the carbon in the ferrouranium was low. Carbon could not be removed from an alloy containing more than the allowable amount by using either iron oxide or uranium oxide, as can be done in other ferroalloys high in carbon. When this was attempted, the uranium in the alloy oxidized and went into the slag, leaving pig iron in the furnace. Keeney[4] was unable to get a ferrouranium containing as much as 30 per cent uranium, and, in addition, the carbon content was too high. He was, however, able to get a commercially high-grade uranium metal as described above. Gillett and Mack[5] succeeded in making a satisfactory ferrouranium by using a pure UO_2, a low-ash coke, and a pure iron as raw materials, with calcium fluoride as slag former. They stated that, by using a tilting direct-arc type furnace with water-cooled magnesite hearth and sides, it should be possible to produce commercially, without a second refining operation, ferrouranium of any desired uranium content, say 40 to 70 per cent, with C averaging below 2 per cent, Si below 0.75 per cent, V below 0.5 per cent, and with Al, S, P, and Mg all so low as to be negligible.

Uses of Uranium.—Besides its use in steel, uranium has been used for many years as a coloring agent for glass. Sodium uranate is usually desired, although uranium oxide is sometimes used as a substitute. The color produced is opalescent yellow, turning green by reflected light. Usually about 20 per cent of uranium calculated as oxide is required to produce the color, thus making the glass quite expensive. Uranium salts are also used in the ceramic industry and produce yellow, orange, and black glazes. The coloring power is great, and only small quantities are required. Uranium salts have also been used to some extent as mordants for silk and wool, and also as a catalyst in the synthesis of ammonia from nitrogen and hydrogen.[6] In

[1] *Compt. rend.*, Vol. 116, p. 347, 1893.
[2] MOISSAN, *Compt. rend.*, Vol. 122, p. 1088, 1896.
[3] *Bull. A.I.M.E.*, August, 1918, p. 1354.
[4] *Bull. A.I.M.E.*, August, 1918, p. 1353.
[5] *Jour. Ind. Eng. Chem.*, Vol. 9, p. 432, 1917; *U. S. Bur. Mines Tech. Paper* 177.
[6] HABER and LE ROSSIGNOL, *Z. Elektrochem*, Vol. 19, p. 53, 1913.

photography, uranium nitrate has been used as a sensitizing agent for paper. With potassium sulphocyanide it can be used for toning bromide prints.

Since Keeney and Gillett made ferrouranium and commercial uranium metal, some interest developed for a time in connection with uranium steel. One firm in this country had ferrouranium on sale and actively cooperated with one or two steel manufacturers in the manufacture of uranium steel. One part of uranium is supposed to replace 2 to 3 parts of tungsten in high-speed steels. Keeney[1] states that ferrouranium can be added to steel in quantities up to 4 per cent with a uranium recovery of at least 50 per cent; and a recovery of 70 per cent can be made in steel containing less than 2 per cent uranium. A considerable portion of the carbon and silicon in the ferrouranium seems to enter the steel. For a steel containing less than 2 per cent uranium, the ferrouranium can be added in the ladle, but a higher percentage of uranium in the steel requires addition in the furnace, or chilling will occur. These results were obtained in the electric furnace, but uranium can also be made in the crucible furnace. Uranium steel has not come into general use, although some of the steelmakers have claimed that uranium is a satisfactory substitute for tungsten in certain cases.

Analytical Methods for Uranium.—A number of methods are suitable for the analysis of uranium ores, and these are discussed at length in *Bulletin* 212 of the U. S. Bureau of Mines. The following short method is usually satisfactory.

Take a 2- to 5-g. sample, ignite if it is carbonaceous, add 16 cc. of 1:1 sulphuric acid and a few drops of nitric acid, and heat till fumes of sulphur trioxide appear. Cool, dilute to 100 cc., add an excess of sodium carbonate and hydrogen peroxide, boil 10 min., filter, and wash with hot water. The iron precipitate should be washed back in the beaker, digested with fresh soda solution, and refiltered, combining the filtrates, which are then acidified with sulphuric acid. After boiling off all CO_2, 2 g. of ammonium phosphate is added, the solution is made slightly alkaline with ammonia, and then barely acidified with acetic acid. The precipitate is gently boiled for 10 min., filtered, and washed thoroughly with a hot 2 per cent ammonium sulphate solution. For accurate work, the precipitation may be repeated. Dissolve the precipitate in 1:4 sulphuric acid, and wash to a volume of 100 cc. Add an excess of potassium permanganate and 10 cc. sulphuric acid, and after warming a few minutes add 5 g. of granulated zinc. Reduce hot for 10 min., cool, filter through glass wool, washing to a volume of 250 cc. with cold water. Titrate with $0.05N$ permanganate. The iron value of the permanganate times $2.5176 = U_3O_8$.

TUNGSTEN

(Atomic weight = 184)

Occurrence.—There are four reasonably common tungsten minerals found in the United States. Ferberite, wolframite, and hübnerite are closely associated as regards their composition. Ferberite is usually classed as an iron tungstate, although it may and often does carry moderate quantities of manganese. Wolframite is an iron-manganese tungstate, carrying usually, however, more iron than manganese. Hübnerite is a manganese-iron tungstate containing more manganese than does wolframite. These minerals form a complete series with almost an infinite number of members between a pure iron tungstate and a pure manganese tungstate. Scheelite, calcium tungstate, is the fourth. It is now the most important tungsten ore. It is easily identified by a blue fluorescence in ultraviolet light. This method of detection is very useful in prospecting and mining scheelite.

[1] *Bull. A.I.M.E.*, August, 1918, p. 1366.

Hess[1] has suggested the following definitions: "Ferberite should be considered as an iron tungstate, $FeWO_4$, contaminated by not more than 20 per cent $MnWO_4$, a proportion equivalent to 4.69 per cent MnO, or 3.63 per cent Mn in the pure tungsten mineral. Hübnerite should be considered as manganese tungstate, $MnWO_4$, contaminated by not more than 20 per cent $FeWO_4$, a proportion equivalent to 4.74 per cent FeO, or 3.69 per cent Fe. Wolframite should cover the ground between the limits above indicated. That is, wolframite should be considered a mixture of iron and manganese tungstates containing not less than 20 per cent nor more than 80 per cent of either. Except the light-colored hübnerites, most of these minerals cannot be detected by the eye or by simple tests, and in the absence of analyses it is, therefore, convenient to refer to the dark minerals of the series as wolframites." Ferberite and wolframite, when pure, are black. When partly oxidized they may appear brownish from the presence of iron oxide. Hübnerite is characteristically brown, some specimens, however, being yellowish, others reddish, and some nearly black. These minerals are all monoclinic in form. Ferberite has more of a tendency to form well-defined crystals than do the others. In hardness, all these minerals are a little over 5. Their specific gravities range from 7.2 or 7.3 in hübnerite to 7.5 in ferberite, while the specific gravity of wolframite is intermediate between these figures. Scheelite is a calcium tungstate, $CaWO_4$. In color it is usually white, light gray, or light yellow, although its color may occasionally vary from greenish yellow to brown. Its luster is slightly glassy. It is found in granular masses, or in irregular lumps of a more or less coarse texture. Its hardness is a little less than 5, and its specific gravity is approximately 6. It possesses four directions of good cleavage. Other tungsten minerals of less importance are stolzite or lead tungstate, cuprotungstite or hydrated copper tungstate, and tungstite or tungstic ocher, a hydrated tungstic oxide.

Ferberite is found in several western states, but mainly in Colorado in the Boulder district. This district has a length of 12 miles in a northeast and southwest direction, and a width of about 7 miles, and begins about 6 miles due west of the town of Boulder. The tungsten veins are in many ways similar to the gold veins of the district and seem to have a close connection with them in genesis. Hübnerite and wolframite are mainly found in New Mexico, Arizona, Nevada, and South Dakota, although the minerals are frequently met with in small quantities in other states. They do not form so important a commercial source of tungsten as ferberite and scheelite. Concentrates of the latter mineral are produced in California near Atolia, San Bernardino County, and also in Inyo County near Bishop. For many years the Nevada-Massachusetts Co. has been the largest domestic producer from mines in Humboldt County, Nevada. Recent search for strategic minerals by government geologists and engineers has revealed a large deposit of high-grade scheelite in the Yellow Pine District, Valley County, Idaho. Scheelite concentrates are recovered as a by-product of gold ores from the Jardine mine in Park County, Montana. Wolframite is mined and concentrated in Stevens County, Washington. Domestic production of tungsten falls far short of our needs, and imports of concentrates are received from the following sources listed in the order of importance: China, Bolivia, Argentina, Australia, Portugal, Thailand, Peru, Mexico, Burma, India.

Extraction from the Ores.—Up to recent years, most methods of treatment of tungsten ores were small modifications of the original Oxland process, which was patented in 1847. This involves a fusion with sodium carbonate of the finely ground ore previously leached with hydrochloric acid to get rid of traces of bismuth if this metal is present. Sometimes a small amount of sodium nitrate is added to the sodium carbonate. The mixture is placed in a reverberatory furnace and sintered, care being taken not to fuse it. It is then removed and ground. Frequently, this

[1] *U. S. Geol. Survey Bull.* 652, p. 22.

treatment does not give a sufficiently high extraction of the tungsten, and involves a second sintering process. The sintered mass is leached with hot water in tanks. Tungsten dissolves as sodium tungstate, while the iron, calcium, and most of the manganese remain insoluble. Some of the phosphoric acid and silicic acid also dissolve as silico- and phosphotungstates. Traces of manganese may also dissolve, owing to the sodium nitrate present, as sodium manganate. The solution of sodium tungstate may be either evaporated to dryness, or evaporated to the point at which crystallization takes place. The chief impurities are sulphates, silicates, and arsenates of sodium, with traces of iron and manganese. Iron, manganese, and arsenic are precipitated by a small quantity of caustic soda, and the greater portion of the sodium sulphate will crystallize out before sodium tungstate. The silica remains in the mother liquor, after the crystallization of the sodium tungstate, and causes some loss of tungsten in the form of soluble silicotungstates, which, however, can be used as by-products for fireproofing purposes. The fairly pure sodium tungstate is redissolved in boiling water and added to a boiling solution of hydrochloric acid made up of 1 part of concentrated acid and 7 of water. Sometimes about 5 per cent of nitric acid is added. The result is the precipitation of the tungsten as hydrated tungstic oxide, which is filtered off and washed in filter presses. It is important that the oxide should be washed free from sodium salts, as otherwise on drying it has a greenish tinge which is not attractive to purchasers.

One of the best methods, if not the best, for producing a high-grade tungstic acid is that of Ekeley and Stoddard.[1] This process is used at one mill in Boulder County for the treatment of medium-grade ferberite ores and concentrates. Usually middlings from the mills, or ore running 15 to 25 per cent WO_3, are used. The product is a high-grade tungstic acid, said to contain less than 0.03 per cent phosphorus and 0.03 per cent sulphur, with only a small percentage of silica. After drying, the oxide runs 99 to 99.7 WO_3. The ore is mixed with sodium carbonate and salt, and the charge is placed in sheet-iron pans 2 × 4 ft. and 6 in. in depth. This is placed in a firebrick furnace heated by oil burners. The charge is so proportioned that a glass slag is obtained. The heat-treatment requires about an hour, at the end of which the pans are pulled out of the furnace onto an iron rack, clamped, and inverted, and the fused charge dumped into an iron receptacle, where it is allowed to cool. It is broken into pieces and ground in a crusher to approximately ½-in. size. It is then mixed in a cement mixer with a hot-water wash liquor from a previous run. The contents are dumped into a screen-bottom trough, which retains the coarse residue. This is shoveled back into the mixer and washed with hot water, the wash water being used in the next run. The concentrated solution is allowed to settle, and the clear solution is given a secret treatment, which removes the last traces of the phosphorus, arsenic, silica, and other deleterious substances. This probably involves the use of magnesium chloride as a precipitant. After filtering, the clear solutions are run into a large wooden tank, heated, and calcium tungstate is precipitated by the addition of a solution of calcium chloride. The precipitate is allowed to settle and is scraped out and treated with commercial hydrochloric acid in a wooden revolving drum. After settling, the solution is drawn off through suction filters. The residue is treated twice with hydrochloric acid in this manner, and finally the whole is dumped onto the suction filters. This treatment produces tungstic acid as a precipitate, and the acid solution contains calcium chloride and calcium sulphate. This is allowed to run into stone vessels, in which the calcium sulphate crystallizes out, and the clear solution is drawn off into barrels, to which lime is added, which produces calcium chloride for further use.

[1] U. S. patents 1255144 and 1322485.

Acid leaching methods are also used in connection with all the commercial tungsten ores. They are especially used for getting rid of manganese, and give good results with scheelite. Ferberite, wolframite, and hübnerite are soluble in hot concentrated hydrochloric acid, but it is necessary to digest the ores in the acid for a considerable time. Under such conditions the ores are decomposed and the manganese goes into solution, while the tungsten is precipitated as tungstic acid and remains with the insoluble residue. After filtering, the residue is extracted with ammonia, which dissolves the tungstic acid, giving ammonium tungstate. On ignition, this is decomposed, giving tungstic acid and ammonia, which may be recovered for further use. Phosphorus is gotten rid of at some stage in the operation by precipitating with magnesium chloride, or, if tungsten powder is made from the tungstic acid, a considerable amount of phosphorus can be leached out of the powder with hydrochloric acid. Scheelite is soluble in hydrochloric acid, but one firm adds to the ease of solubility by using hydrochloric acid and sodium chlorate. The decomposition of the ore takes place in acidproof earthenware pots in a hood with a steam draft. After complete decomposition the tungstic acid and insoluble silica are filtered off. By using high-grade scheelite the amount of silica present is not large, and the refining of the product is not carried any further, but the acid, without further removal of the silica, is used for the manufacture of tungsten powder.

Gin[1] suggests a bisulphate fusion for the ore whenever tin is present. This method, therefore, does not apply specially to American ores, but is useful for some of the foreign ores. The tin can be largely separated from the tungsten ore by means of magnetic separation, but there is usually at least 1 per cent of tin oxide left behind with the tungsten. The ore is decomposed by means of acid potassium sulphate in a muffle furnace. After the sulphate is fused, the ore is thrown in, the mass is stirred continually, and the temperature increased until the whole mass is fluid enough to run out of the furnace. After solidification the fused mass is ground and treated with water, which dissolves the soluble sulphates and phosphoric acid and leaves insoluble potassium acid tungstate as a white amorphous precipitate. About 50 per cent excess of bisulphate over that theoretically required is actually necessary. The insoluble residue is dried and treated with a warm solution of ammonium carbonate, or cold ammonia water in which carbon dioxide is passed. The potassium acid tungstate dissolves leaving the silica, the cassiterite, and the insoluble sulphates. The solution is evaporated to crystallization, which gives ammonium tungstate, from which tungstic oxide is made by heating.

Concentration Methods.—Tungsten minerals have high specific gravities and are readily concentrated by jigs and tables. They slime badly, and slime tables or "rag plants" were formerly used to limit losses of slimed mineral. Recent advances in the art of flotation are now being applied to the concentrations of scheelite ore with considerable benefit. Scheelite concentrates often contain considerable garnet which is magnetically separated. A roast to remove sulphur is also used in some cases. Milling procedures have been improved and now yield 85 to 90 per cent recovery in a concentrate well above the minimum (60 per cent WO_3) market grade.

Metallic Tungsten.—Metallic tungsten can be made in a number of ways. The purest product is obtained by heating a very high-grade tungstic oxide in a current of hydrogen. The oxide can also be reduced by means of carbon or metallic zinc. Metallic aluminum and magnesium also can be used instead of zinc. Most metallic tungsten prepared commercially is in the form of powder for making tungsten steel. Reduction with carbon is the method usually used, as the reaction goes readily and presents few difficulties. The reduction can take place either in a steel tube or in a

[1] *Trans. Am. Electrochem. Soc.*, Vol. 13, p. 481.

covered steel crucible. Davis[1] has carefully studied the conditions and temperatures necessary for the reduction of tungstic oxide to the metal. He finds that at 650 to 850° the oxide goes to a black or purple on heating with carbon; at 950 to 1050°C. a chocolate-colored product is the result (probably WO_2); and at temperatures above 1050°C. the gray powdered metallic tungsten results. The ratio of tungstic oxide to carbon varies from 10:1 to 10:1.6, depending on the process used, the temperature of reduction, and the time involved. A small excess of carbon can be partially removed by washing. Both fire-clay crucibles and iron tube give satisfactory results, and a product of over 98 per cent metallic tungsten can be produced. Whereas the reduction to metal is complete at 1050°C., it is better to keep the temperature around 1100°C.

Shapely's process for producing commercial tungsten is thus described:[2] A scheelite concentrate is mixed with crude soda (trona) in a ball mill, and the batch transferred to a firebrick crucible and melted with crude oil fuel, the flame striking directly on the charge. When the melt is quiet, the charge is tapped, the molten material flowing directly into a small Pachuca tank nearly filled with water. The water is agitated violently by compressed air during the pouring of the charge and for an hour in addition. The action of the water on the molten sodium tungstate shatters this material so that it will all pass a 20-mesh screen and the sodium tungstate is easily and completely dissolved. The charge from the Pachuca is transferred to a redwood filter tank having a filtering medium of coco matting and canvas. The filtrate runs to storage tanks through a small filter press having filter paper between the plates. An absolutely clear solution results and, as the amount of insoluble matter is small, the press is cleaned only at rare intervals. The material in the filter tank is washed several times and the wash water returned to be used for the next melt.

To precipitate an easily filterable tungstic oxide, the solution is brought to boiling by means of steam coils placed directly in the solution, and the boiling solution is transferred to stoneware crocks. The crocks are jacketed for hot water and contain enough hydrochloric acid to precipitate the tungsten as oxide. (About 3 per cent of nitric acid is used with the hydrochloric.) If the solution is kept nearly at the boiling point, the precipitate will be comparatively coarse grained and easily filtered.

The precipitated material is allowed to stand for an hour at a temperature close to 100°C., and the clear, weak acid solution decanted and replaced with distilled water obtained from the heating coils. The precipitate is run into a flat-bottomed filter tank having a filtering medium of coco mat and canvas (protected with shoveling strips) and is washed repeatedly with distilled water. An acid-free product results, containing about 45 per cent water, as determined by heating a sample to 500°C.

The batch is then transferred to a wooden mixer similar to a butter churn, and the correct amount of gas-house carbon is added to reduce the tungsten oxide to the metal. After kneading for half an hour, the mixture is transferred to fire-clay crucibles and allowed to dry slowly, waste heat from the reduction furnace being used to dry the product completely. Any reduction in volume due to shrinkage during drying is made up with more dry material, and the crucibles are covered with a graphite lid, ground to fit.

Reduction is done in a special furnace, which is operated continuously and reduces a charge in about a 4-hr. heating at 1250°C. Fuel oil is used for heating the furnace.

The metallic tungsten is a lumpy gray mass that must be ground and screened, and packed in 100-lb. tins.

The process used by the Fansteel Products Co. uses a hand-picked wolframite ore which is charged in a small reverberatory, 200 lb. ore to 100 lb. soda ash. The

[1] *Jour. Ind. Eng. Chem.*, Vol. 11, No. 3, p. 201.
[2] *Chem. Met. Eng.*, Vol. 24, p. 374, Mar. 2, 1921.

charge is hand rabbled at 800°C., which converts all manganese oxide to dioxide, while the following main reaction takes place:

$$2FeWO_4 + O + Na_2CO_3 = 2Na_2WO_4 + Fe_2O_3 + 2CO_2$$

The temperature must be kept low enough not to fuse the mass. The furnace bottom is now a 1-in. iron plate, but basic brick is recommended.

The furnace product is leached, and the sodium tungstate solution at 30 to 50°Bé. is brought to boiling and 20°Bé. calcium chloride solution added. The calcium tungstate thus produced is washed by decantation and is then boiled by means of live steam with hydrochloric acid, thus producing tungstic acid.

This tungstic acid is then converted to ammonium paratungstate and the ammonia removed by nitric acid. Reference to the original article should be made for details of this process.[1]

Davis also found that the temperature of reduction with hydrogen at ordinary pressures is much the same as with carbon. The properties of metallic tungsten are unique, so that when it was first prepared it led to a search for methods for producing the metal in a ductile form. It was found that this could be done by repeated heating, rolling, hammering, drawing, and swaging. Cast tungsten, or tungsten powder, differs widely in its properties from the pure raw material, such as is used in the manufacture of incandescent-lamp filaments. The tungsten powder is brittle, crystalline, and hard and has a specific gravity of 16 to 17. The pure metal is softer and tougher and can be welded at a yellow heat, even drawn into fine wire. Its specific gravity is 19.3 or over, and the melting point close to 3270°C. A wire of 5-mm. diameter has a tensile strength of more than 450,000 lb. to the square inch. At a red heat, the metal oxidizes in air. Melted sulphur and phosphorus attack it slowly; potassium bisulphate, caustic alkalies, and fused nitrates attack the metal, but solutions of these salts have practically no action on it. Hot dilute sulphuric acid affects it only slightly, but the concentrated acid dissolves the metal slowly. At ordinary temperatures hydrochloric acid of any concentration has practically no action, but the strong boiling acid dissolves it slowly. Concentrated nitric acid and hydrofluoric acid have very little action on tungsten, but the two acids when mixed attack it fairly rapidly.

Ferrotungsten.—Tungsten is the principal rare metal used for alloy purposes in connection with the manufacture of high-speed steels. In making this steel, either ferrotungsten or tungsten powder may be used. The annual production of the two is probably about equal in quantity. When ferberite is used, practically all ferrotungsten is made directly from the high-grade concentrate without previous chemical treatment of the ore. The product obtained in such a case contains usually 70 to 85 per cent W, 0.5 per cent C, 0.4 per cent Si, 0.5 per cent Mn, 0.01 per cent S, and 0.02 per cent P. Ferrotungsten has a high density and fine gray fracture, and is not crystalline.

Keeney[2] gives a detailed description of the manufacture of ferrotungsten. The reduction with carbon goes readily. The slag may contain as high as 8 per cent FeO, but less than 1 per cent WO_3. Theoretically, the reduction of 100 parts of alloy from 122 parts of ferberite requires 16 parts of carbon, but practically about 25 per cent excess of carbon is charged. Small amounts of lime and fluor spar are used to flux the silica. Operating in this manner, with an excess of carbon, a product is made containing 3 per cent C, 70 per cent W, 0.05 per cent P, and 0.01 per cent S, with slag containing below 1 per cent WO_3. The analysis of a typical concentrate for the manufacture of such a product is WO_3, 60.36; Fe, 22.0; SiO_2, 8.0; Mn, 0.05; S, 0.35; and P, 0.05 per cent.

[1] *Chem. Met. Eng.*, Vol. 22, p. 9, Jan. 7, 1920.
[2] *Bull. A.I.M.E.*, August, 1918, p. 1338.

A typical operation involves charging into the furnace 65 lb. of a mixture composed of 200 lb. concentrate, 42 lb. coke, 56 lb. lime, and 6 lb. fluor spar. Three more 65-lb. charges are added at intervals of ½ hr., and at 2½ hr. from the start the furnace is tilted and the slag poured. This cycle is repeated until a 1200-lb. button has been formed, requiring 24 to 36 hr. The furnace is allowed to cool, is torn down, and the button of metal removed, cleaned, and broken up. This crude metal is refined as follows: A charge of 150 lb. metal and 75 lb. ferberite concentrate is smelted for ½ hr., when 12 lb. of fluor spar is added. After another 3 hr. the slag is poured and a fresh charge is started. The process is continued for 36 to 48 hr. until a button weighing 1500 lb. has been formed, when the furnace is allowed to cool, is torn down, and the button of metal removed, cleaned, and broken. Ferrotungsten containing less than 1 per cent carbon can be made in a single smelting operation by careful regulation of the carbon in the charge and the use of an acid slag. The product, however, is less pure and the slag loss is higher. In addition, the metal will contain more phosphorus and sulphur.

Tungsten Carbide.—Tungsten carbide is nearly as hard as a diamond, but it is so brittle and hard to prepare in massive form that no use was made of this property until recently. By a method developed in Germany, fine crystals of tungsten carbide are mixed with powdered cobalt, pressed into small bars, and sintered to produce most remarkable tips for machine tools. Although the amount of tungsten thus used is small, carbide-tipped tools have had a profound effect on the machine-tool industry. They can be used to machine hardened steel, glass, porcelain, plastics, and many other substances that were formerly cut only with diamond points. The carbide tips are much more rugged than a diamond and are not injured when cutting plastics with metal inserts. With these tools the cutting speed of lathes can be increased many fold, and much less time is required to maintain a sharp cutting edge.

Uses of Tungsten.—The main use for tungsten is in the manufacture of steel, especially high-speed steel. Such steel is generally made by the crucible process, although not always. A steel suitable for such use may contain as high as 15 or 20 per cent tungsten, and as low as 8 or 10 per cent tungsten, and 4 per cent chromium. Vanadium and molybdenum may also be used in small quantity, and uranium has in some special steels partially replaced the tungsten. Tungsten is also used in self-hardening steels, or those requiring no tempering after forging. They may have a composition between the following limits: W, 2.4 to 3.4 per cent; Cr, up to 6 per cent; C, 0.4 to 2.2 per cent; and Si, 0.2 to 3 per cent.

The chief property that tungsten gives to steels is tensile strength, which, with the elastic limit, increases within certain limits as the percentage of tungsten increases. Elongation and resistance to shock diminish proportionately, and the hardness increases fairly consistently with the percentage of tungsten. Tungsten is also used for filaments in electric lamps. For making the filaments, the "squirting" process was originally employed. This involved mixing metallic tungsten powder with an organic binding material, such as gum, and these were squirted into the filament. The carbon was eliminated by placing the filament in an atmosphere containing a volatile compound of tungsten, such as the oxychloride, and a small quantity of hydrogen. On heating the filament by an electric current, the carbon was replaced by tungsten.

Another method consists in mixing metallic tungsten powder with an amalgam containing equal amounts of cadmium and mercury and squirting the mixture through a die in the usual way. The cadmium and the mercury in the filament are volatilized by heating, and the filament retains the usual brittleness, but after continued heating at higher temperatures the filament becomes pliable and can be bent. Drawn filaments are now used, the drawing being made possible by hammering, heating, swaging, etc. Tungsten is also a constituent in the so-called "bronze powders" employed

for decorative purposes, and has also been used to a small extent in the fireproofing of cloth and other fabrics, as a mordant for silk, and for coloring glass and porcelain.

Analytical Methods for Tungsten.—Tungsten in ores can be determined quantitatively by the following method: The ore ground as finely as possible in an agate mortar is fused with five to ten times its weight of sodium potassium carbonates and extracted with hot water. If any gritty particles remain, another fusion is necessary. An equal volume of concentrated hydrochloric acid is added to the aqueous solution of the alkaline tungstate, and the whole evaporated to dryness, after which the silica is dehydrated by heating at 120°C. for an hour. The residue is moistened with hydrochloric acid, taken up with water and boiled, then filtered and washed with 5 per cent HCl or ammonium nitrate solution. The filtrate contains a small amount of tungsten, which is determined by heating the filtrate and the washings to boiling and adding 5 to 6 cc. of a cinchonine solution, made by dissolving 25 g. of cinchonine in 200 cc. of 1:1 HCl. This is allowed to digest on a hot plate, while the other operations are being performed.

The precipitated tungstic oxide is dissolved in hot ammonia solution (Watt's solution of 200 cc. of strong ammonia, 1000 cc. of water, 10 cc. of HCl), filtered into a platinum dish, in which the filtrate and washings are evaporated to dryness and ignited. The cinchonine precipitate is filtered and washed with hot dilute cinchonine solution (100 cc. water to 5 to 6 cc. of the above solution), dried, and ignited in the platinum dish with the tungstic oxide. A few drops of sulphuric acid and a little HF are added, and the SiO_2 driven off at a dull red heat. The tungsten is weighed as WO_3. Small quantities of impurities may be removed by treating the WO_3 with the ammonia solution, filtering, and again igniting.

Ferrotungsten can be analyzed by the following method, which was used at the laboratories of the Tungsten Products Co. at Boulder, Colo.

The refined ferrotungsten, crushed and rolled to pass a ½-in. mesh screen, goes to a machine which automatically mixes, samples, and sacks the product for shipment. The sampler is of a type developed by this company, which cuts one-fifth of the total mix. This cut passes through the machine again after being rolled to approximately ¼-in. mesh. If the original mix is very large, the operation is repeated to bring the weight of the sample down to less than 500 lb. This final sample from the automatic is passed repeatedly through a riffle sampler until the last cut weighs 15 to 50 lb. This goes to the laboratory sampling department, where it is reduced in a steel mortar to pass a 3⁄16-in. screen. The pounding necessary for this process is done by a 2-in. Ingersoll Rand piston drill set up vertically in a frame above the mortar and pestle in such a manner that it is used as an air hammer. The sample is thoroughly mixed and split twice, and one-quarter is then further reduced to pass a 10-mesh screen. This procedure of screening, mixing, and splitting is continued through a series of screens until the last portion passes the 200-mesh screen, giving the analyst about 100 g. of finely powdered metal. The operation of reducing a 20-lb. sample received from the smelter to a 100-g. laboratory pulp of 200-mesh powder by this system requires about 1 hr.

For the determination of tungsten, two 1-g. samples are mixed separately in nickel crucibles with about 5 g. of sodium peroxide and a cover of sodium carbonate. Fusion is done in an electric muffle at about 800°C., which requires 6 to 7 min. to make a perfect decomposition. Cool, leach out in water in covered 400-cc. beakers. Remove crucibles, and acidify carefully with hydrochloric acid, using a moderate excess. Add about 2 cc. nitric acid or H_2O_2 to assist in dissolving any small fragments of nickel oxide scale, and bring to a boil. Most of the tungsten separates as H_2WO_4, and all iron and nickel salts are in solution. Add about 40 cc. cinchonine solution, stir and let stand in a warm place for about 4 hr., or preferably overnight. This precipitates

all the remaining tungsten as cinchonine tungstate, and it has proved to be just as effective a reagent for this purpose as quinine hydrochloride. Filter off the settled precipitate through a 15-cm. close-weave paper arranged over a platinum cone and suction flask. Wash thoroughly with warm dilute cinchonine wash water, using gentle suction. No trouble will be experienced due to the precipitate sticking to the beaker if a few drops of hydrofluoric acid are used.

The washed precipitate is transferred to a shallow gold dish of known weight and ignited to WO_3 in the muffle. Cool, moisten with 10 or 12 drops of hydrofluoric acid to remove any traces of SiO_2 which might be carried down, dry, and ignite again. Weigh and calculate to W. The factor is 0.793. Duplicate determinations carried out in this way should check to within 0.10 per cent. The proportions used in the cinchonine solution are 50 g. of cinchonine alkaloid dissolved in 2 l. of cold water containing 150 cc. of hydrochloric acid; for the cinchonine wash water, 100 cc. of the above cinchonine solution and 50 cc. of hydrochloric acid diluted to 1 l. with hot water and used from a bulb wash bottle is convenient. For the determination of carbon—ferrotungsten and tungsten metal powder burn completely and readily in oxygen—and carbon is easily determined in any type of combustion train. In the laboratory mentioned they prefer to catch the CO_2 in a Meyer bulb in 2 per cent barium hydrate solution, to filter, wash, and weigh the $BaCO_3$.

The usual fusion-oxidation methods of determining sulphur are all open to objections when applied to a ferroalloy or other material whose sulphur content is below 0.05 per cent. The blank is always high, due to traces of sulphates in fluxes and reagents used and the danger of picking up fumes or traces of sulphuric acid from the apparatus of a general laboratory. The sulphur content of ferrotungsten occurs as sulphides, which, in a finely ground sample, are completely decomposed, yielding H_2S. This suggests at once the application of the method which has been used successfully for many years. Two to five grams of 200-mesh ferrotungsten or metal powder is weighed into an evolution flask. Cover with 50 cc. of water, and add 25 cc. of strong hydrochloric acid by way of the separatory funnel. Heat to boiling, and boil for about 10 min., catching the evolved gas, air, and steam in ammoniacal cadmium chloride solution. The usual yellow precipitate of cadmium sulphide shows the presence of sulphides in the alloy. Wash the cadmium chloride solution from the bulbs, then cool, acidify with hydrochloric acid, and titrate at once against a weak iodine solution (1 cc. = 0.0005 g. of sulphur), using starch as an indicator. The iodine solution is standardized by using a government standard steel of known sulphur content, or by using a ferrotungsten of known sulphur content. Boiling with dilute hydrochloric acid does not dissolve the alloy, but does decompose the sulphides present, as may be shown by filtering off the contents of the evolution flask after the operation and examining for sulphur by a fusion method or by a combustion method.

The removal of phosphorus from the alkaline liquor after a fusion decomposition of ferrotungsten presents certain difficulties. Precipitation with magnesia mixture from dilute solutions is incomplete unless much time is allowed for this step, also precipitation from concentrated solutions either as magnesium-ammonium phosphate or as aluminum phosphate tends to drag down some tungsten, involving another step for its removal. To avoid these difficulties, the use of uranium acetate has been introduced at this stage. The precipitation is quantitative from moderately dilute solutions, and no dragging down of tungsten occurs. Weigh a 1-g. sample into a nickel crucible containing 6 to 8 g. of chemically pure Na_2O_2. Mix thoroughly and cover with about 1 g. of chemically pure Na_2CO_3. Ignite in a muffle to complete fusion of the fluxes. Cool and leach out carefully with warm water in a 250-cc. covered beaker. Remove the crucible, and partly neutralize the NaOH with 25 cc. of HCl (1:3) to permit filtering without dilution. Stir and then allow the dense $Fe(OH)_3$ to

settle out while standing on a warm plate. Decant off through a 12½-cm. qualitative paper into a 600-cc. beaker. Wash the precipitate into the filter, allow it to drain thoroughly, then give it two good washes with hot water, stirring up the precipitate well with a fine jet. Reserve this precipitate of $Fe(OH)_3$, which contains a small amount of phosphorus, to add to the uranium precipitate obtained from the tungsten solution.

Acidify the filtrate of sodium tungstate and sodium phosphate with acetic acid, using 30 cc. of 40 per cent acetic. Add 2 cc. of 5 per cent uranium acetate solution. Boil off all CO_2. Make just alkaline with NH_4OH (1:1). This will require about 20 cc. The precipitate is ammonium uranyl phosphate. Add 2 cc. more uranium acetate, which precipitates at once as uranium hydroxide and serves to drag down the last traces of phosphate, as well as to assist in filtering the ammonium uranyl phosphate. Boil off any large excess of NH_4OH. Filter through a qualitative paper, and wash twice with hot water to remove tungsten. Place the precipitate in the same beaker together with the iron precipitate obtained above, add 30 cc. water and 25 cc. strong nitric acid. Boil until both precipitates are in solution and the filters reduced to pulp. Filter into a 500-cc. Erlenmeyer flask, washing the pulp once with hot water. Add 5 cc. of 5 per cent $KMnO_4$ solution to acid filtrate. Boil to oxidize all phosphorus to H_3PO_4. Clear of MnO_2 by adding 2 cc. of H_2O_2 (1:1). Boil to remove excess H_2O_2, and cool under the tap. Add 45 cc. of NH_4OH (1:1), which will nearly neutralize the nitric acid, then 50 cc. of molybdate solution. Stopper the flask, shake for 5 min., and let stand at least 15 min. before filtering. Filter through a 9-cm. filter. Wash with acid ammonium sulphate wash solution to remove all nitromolybdate. Dissolve the yellow phosphomolybdate in hot dilute ammonia water, which must be free from chlorides, into the same Erlenmeyer flask. Wash the paper well with alternate washes of ammonia water and hot water. When cool, acidify with 5 cc. of H_2SO_4 (1:1) and pass through the reductor, following with a thorough wash of cold water. Titrate against standard $KMnO_4$ solution to the same end point as used in determining the reductor blank. The iron value of the standard permanganate solution times 0.0163 equals the P value. The ammonium sulphate wash solution must be distinctly acid. A good formula is H_2SO_4 (1:1), 100 cc.; NH_4OH (1:1), 60 cc.; water, 21. If convenient, it is well to allow the precipitate of yellow phosphomolybdate to stand about an hour after shaking for 2 min. A blank on all reagents, including a fusion of Na_2O_2 and Na_2CO_3, should be carried through with the determinations. It is sometimes desirable to add a measured quantity of dilute phosphate solution of known phosphorus content to the blank for close work. Checks should agree within 0.015 per cent P.

MOLYBDENUM

(Atomic weight = 96)

Occurrence.—The chief commercial minerals of molybdenum are: molybdenite, MoS_2; wulfenite, $PbMoO_4$; and molybdite, $Fe_2O_3.3MoO_3.7\frac{1}{2}H_2O$. Of lesser importance are ilsemannite (possibly $MoO_3.SO_3.5H_2O$); belonesite, $MgMoO_4$; and powellite, $CaMoO_4$. The first three are the only ones from which molybdenum is obtained commercially. Molybdenite contains 59.5 per cent molybdenum and 40.5 per cent sulphur. It is a soft opaque lead-gray mineral with metallic luster. It frequently occurs in flakes or scales, resembling some micas as regards its cleavage. In hardness it ranges from 1 to 1.5, and readily leaves a mark of a bluish-gray color on a paper. Its specific gravity is 4.7 to 4.8. The mineral is widely distributed throughout the United States, especially in the West, and, whereas it is found in a large number of

localities in small quantities, there are also several large deposits which are being worked commercially.

The most important of these is at Climax, Colo., near Leadville. Here a large portion of a mountain is impregnated with the mineral, and, whereas the grade averages less than 1 per cent MoS_2, the amount of ore available is very large. Another large deposit is on Red Mountain, near Empire, Colo., about 50 miles due west of Denver. There are two mills at Climax and one at Red Mountain. Smaller deposits of molybdenite are found in several places in the United States, especially in Arizona, New Mexico, Nevada, California, etc. Wulfenite contains theoretically 26.15 per cent of molybdenum and 56.42 per cent of lead. It is a brittle, heavy, semitransparent mineral with resinous luster and is generally of a wax or orange-yellow color, although occasionally it is olive green, yellowish gray, or even brown. Its hardness is 2.75 to 3, and its specific gravity is 6.7 to 7. It crystallizes in the tetragonal system, and the crystals are commonly square and tabular and sometimes very thin. Less frequently, they are octahedral or prismatic. Like molybdenite, wulfenite is widely distributed in the western states; probably the largest known deposit is at the Mammoth mine, Mammoth, Ariz., from which a very considerable tonnage of concentrates has already been obtained. It is, however, found in numerous other places in Arizona, Nevada, and to some extent in New and Old Mexico. Molybdite is a hydrous ferric molybdate, lemon yellow to pay yellow in color, and occurs as an earthy powder, usually as incrustations. Molybdite is an alteration product of molybdenite, probably formed by the interaction of molybdic acid and limonite, the molybdic acid being an oxidation product of the molybdenite.

Molybdite, therefore, is frequently found associated with molybdenite, especially where the latter mineral has had a chance to weather. Molybdenum minerals are found in notable quantities in several foreign countries. Molybdenite is found in Queensland, New South Wales, Norway, and Canada. Only since 1923 have commercial amounts of molybdenum been produced in the United States, and the world's supply came from Queensland, New South Wales, and Norway. Domestic production has increased from 500 tons in 1925 to over 17,000 tons in 1940; the latter being more than 90 per cent of total world production.

Although Climax has consistently maintained its leading position, the recovery of molybdenum concentrates as a by-product of copper operations at Bingham, Utah, Chiro, New Mex., and Miami, Ariz., has become increasingly important and amounted to 30 per cent of domestic output in 1940. The recovery at Chiro is described in the *Engineering & Mining Journal*, Vol. 140 (September, 1939) as follows: The concentrate from the cleaner cells carries about 30 per cent Cu and 0.5 per cent Mo. It is freed from reagents by steam, reconditioned, and the MoS_2 floated out. The tails carry 30 per cent Cu, 0.06 Mo.

Extraction from the Ores.—As ferromolybdenum, which is the chief use for molybdenum, can be made directly from molybdenite concentrates, it is not necessary to treat molybdenite chemically unless molybdic oxide or ammonium molybdate are required for chemical purposes. In the latter case, the molybdenite may be roasted to oxide, treated with ammonia, which dissolves the molybdic oxide as ammonium molybdate, filtered, and evaporated to dryness, or to crystallization of the ammonium molybdate. On ignition the ammonia is driven off and may be recovered for further use.

Climax Conversion Practice.—The present practice of the Climax Molybdenum is described by E. S. Wheeler as follows:[1] The 12-hearth roasting furnaces at Langeloth have been arranged so that the reaction gases can be withdrawn from each hearth from the eighth up separately, while air can be admitted in any desired quantity on

[1] *A.I.M.M.E. Tech. Paper* 1718, February meeting, 1944.

each hearth from the third to the seventh. As a result, it is possible to keep the hearth temperatures down to about the subliming temperature of molybdenum oxide (1100°F.) with great increase in furnace capacity, better recovery of the oxide, and greatly decreased furnace repairs. About 30 per cent of the roasting furnace production is sold as "technical molybdic oxide" carrying 56 to 62 per cent Mo; 5 to 11 per cent insoluble; 0.5 to 1.0 per cent Fe; and small amounts of sulphur, copper, lime, and zinc.

Calcium molybdate was originally prepared at Langeloth by mixing roasted concentrates with quicklime and water and heating to form a technical molybdate containing about 40 per cent Mo. It was later discovered that if uncalcined pulverized limestone of high purity was thoroughly mixed with the roasted concentrates, the product was suitable for direct addition in steel furnaces.

Molybdic oxide briquettes are an important item in the Climax production. Concentrates of known molybdenum content are thoroughly mixed with air-floated pitch and the mixture fed by gravity to hydraulic briquetting presses, which have a combined capacity of 60,000 to 80,000 lb. Mo. per day. The average briquette pressure is 10,000 to 11,000 lb. per sq. in., but a pressure of 18,000 lb. can be applied. The briquettes are 4 in. in diameter and 4 to 4½ in. long, and the mold liners are chromium-plated on the inside to withstand abrasion. The liners require replating about each 100,000 briquettes.

Molybdic oxide is prepared by heating technical oxide to about 1800 to 1900°F. Air is drawn in over the heated surface and sweeps the MoO_3 into a metal flue leading to a bag filter where the pure oxide is collected. The tailings from this process are sent back to use as raw material in other processes.

Ferromolybdenum is still produced by the Thermit process. A typical mix is 1300 lb. molybdenum as oxide, 116 lb. low-grade aluminum, 1122 lb. ferrosilicon (50 per cent grade), 618 lb. iron ore (69 per cent grade), 160 lb. lime, and 50 lb. fluor spar. The mixture is run into a brick-lined steel shell and the reaction started by igniting the charge with a mixture of aluminum and sodium peroxide. The reaction requires about 20 min., after which the slag is tipped off with the exception of a thin protective layer and the metal given 4 to 6 hr. to solidify.

Wulfenite presents a more difficult metallurgical problem than molybdenite. This mineral nearly always carries small quantities of vanadinite, and the two cannot be separated mechanically. Kissock first used a sodium carbonate fusion method in a small blast furnace. The wulfenite, mixed with sodium carbonate and coke, was strongly heated, and the lead was obtained as metallic lead, while the molybdenum went into the slag in the form of sodium molybdate. This slag was used directly in the electric furnace for the making of ferromolybdenum, but the excess of sodium carbonate had very decided and deleterious effects on the furnace linings. Holladay prepares a sodium molybdate slag reasonably free from lead and other impurities, then leaches the slag with water, and adds dilute calcium chloride solution in the cold. This precipitates most of the impurities that are still present, while the molybdenum stays in solution. On filtering and boiling and adding excess calcium chloride, the molybdenum is precipitated as calcium molybdate, which can be used for the preparation of molybdic oxide or can be used directly in the making of molybdenum steel. Conditions for the precipitation of calcium molybdate have been studied carefully by Bonardi.[1]

Concentration Methods.—Molybdenite can be concentrated readily by flotation methods. An ore carrying less than 1 per cent can be concentrated to a product carrying 60 or even 70 per cent molybdenite. Usually, mixtures of kerosene and pine oil are used, although other oils give satisfactory results on certain ores. Wulfenite

[1] *Chem. & Met. Eng.*, Sept. 15, 1919.

can be concentrated by ordinary milling methods, using tables and slimers. The mineral crushes readily, but an ore carrying as little as 0.5 per cent MoO_3 as wulfenite can be concentrated with a fair recovery. Vanadinite, which is frequently associated with it, cannot be separated to form very satisfactory products, as the specific gravities of the two minerals are almost the same.

Metallic Molybdenum.—Metallic molybdenum may be prepared by reducing molybdic oxide with aluminum powder or by heating the trioxide or one of the chlorides in a current of hydrogen. It may also be prepared by heating a mixture of molybdenum trioxide with one-tenth of its weight of sugar charcoal in an electric furnace in a carbon crucible. The pure metal is malleable and is not hard enough to scratch glass. It has a specific gravity of about 9 and can be forged when hot. It oxidizes readily at a dull red heat and is attacked by fused potassium chlorate, nitrate, etc.

Ferromolybdenum.—The raw materials for ferromolybdenum may be molybdenite, molybdic oxide, a sodium-molybdate slag, or calcium molybdate. The reducing agent is usually carbon, although 90 per cent silicon material ground to 60 mesh has been used. Lime and fluor spar are used as fluxes. The reaction that takes place with molybdenite is as follows:

$$2MoS_2 + 2CaO + 3C = 2Mo + 2CaS + 2CO + CS_2$$

Reduction with silicon metal gives the following reaction:

$$MoS_2 + Si = Mo + SiS_2$$

According to Keeney,[1] for about 100 parts of molybdenite, 58 parts of lime are necessary for slagging the sulphur as calcium sulphide. The reaction works close to the theoretical, and there is no difficulty in making a product with about 0.1 per cent sulphur and 1½ to 3 per cent carbon. With sodium molybdate slag, the reaction is as follows:

$$Na_2MoO_4 + 3C = Mo + 3CO + Na_2O$$

The reduction of sodium molybdate requires considerably more power than the reduction of the sulphide or oxide. The average power consumption is 7 to 7½ kw.-hr. per lb. of molybdenum produced. The recovery varies from 78 to 80 per cent with a loss of 10 per cent in the slag and 10 per cent mechanically by volatilization. Ferromolybdenum containing 80 per cent molybdenum and under 1 per cent carbon cannot be regularly tapped from the electric furnace.

Production of molybdenum alloys by the direct addition of calcium molybdate to the molten steel is rapidly replacing the use of ferromolybdenum. Other similar molybdate compounds or briquettes of molybdic oxide have also been used. These direct methods are more economical because one furnace operation is eliminated and less molybdenum is lost in slags. The molybdenum compounds are reduced to metal in the steel bath by the same reactions that are used for production of ferromolybdenum.

Uses of Molybdenum.—Molybdenum is used chiefly to make special alloy steels, usually in combination with other alloying elements. In many cases, it is substituted for strategic metals, such as tungsten, nickel, and manganese, since ample supplies of molybdenum are available in the United States. Alloy steels containing molybdenum are finding increasing use in the aircraft, automotive, and railroad industries. The amount of molybdenum in such steels varies from 0.2 to 3 per cent, but rarely above 1.5 per cent. The newer developments include the addition of molybdenum to a 3 per cent chromium steel used for crankshafts, a nitriding steel containing

[1] *Bull. A.I.M.E.*, August, 1918, p. 1334.

chromium, molybdenum, and nickel (but no aluminum), and a steel containing 2 per cent chromium—0.50 per cent molybdenum used for lining cylinders of aircraft engines. Molybdenum steels are used by railroads in tires, car wheels, flues and cylinders, also nickel-chromium molybdenum steel for rods, pistons, axles, shafts, and pins. Such steels are largely used in oil-well drilling and oil-refining equipment. Molybdenum alloy steel for high-speed cutting tools and dies is receiving increased attention.

Molybdenum compounds are used in the chemical and ceramic industries, but the consumption in these expanding fields is not large.

Analytical Methods for Molybdenum.—The following is a revision by Doerner of the method of Bonardi and Barrett of the U. S. Bureau of Mines. Take a 0.25- to 5.0-g. sample of finely pulverized ore, add 15 cc. HNO_3, and heat until the brown fumes are gone. Carefully add 10 cc. HCl and heat 20 min., or until decomposition is complete. If much lead is present, as in wulfenite, take to fumes with 10 cc. H_2SO_4, cool, dilute to 60 cc., and heat to dissolve soluble sulphates. Cool and filter off the lead. Add an excess of ammonia and 5 cc. of magnesia mixture. If much calcium is present, add 5 g. of Na_2CO_3. Boil 10 min. and filter, washing well with hot water. If the precipitate is large, dissolve it in HCl and repeat the precipitation.

In rare cases molybdenite is not dissolved by acids. Fusion with a Na_2O_2 and Na_2CO_3 mixture is then necessary. The melt is dissolved in water and filtered. The filtrate is saturated with H_2S and barely acidified with HCl. Heat to boiling, filter, and wash with hot water. Dissolve the MoS_2 precipitate in 1 to 1 HNO_3, and take to fumes with 10 cc. of H_2SO_4. Cool, dilute, filter, and make alkaline with ammonia. The solution should be about 250 cc. in volume. Make acid with HCl, using methyl orange as an indicator, and add 5 cc. in excess. Add 5 to 10 g. of sodium-ammonium acetate. The addition of 8 drops of HNO_3 is recommended by Weiser.[1]

Titrate hot with lead acetate solution (about 18 g. of crystallized salt per liter) until a test drop gives no color with a drop of tannic acid solution. For accurate work or to standardize the solution, add 2 cc. excess of lead acetate, heat 20 min., and filter, washing well with 2 per cent NH_4NO_3 solution. Ignite the precipitate and filter in a fire-clay annealing cup in a muffle at dull-red heat. The weight of the $PbMO_4$ precipitate times 0.2615 = Mo.

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[1] *Jour. Phys. Chem.*, Vol. 20, p. 640, 1916.

CHAPTER XXIII

METALLURGY OF RADIUM AND URANIUM

By H. A. Doerner[1]

Occurrences.—As uranium is the mother of radium, the two elements are always found together as uranium minerals. Therefore the metallurgy of these related elements is unavoidably connected and must be treated in the same chapter. Uranium considered as a ferroalloy material, however, has been treated in the preceding chapter.

Uraninite, better known as pitchblende, and carnotite are the most important radium ores. Pitchblende is uranium oxide (UO_3, UO_2) of indefinite composition containing variable amounts of Pb, Ca, Fe, Bi, Mn, Cu, Si, Al, rare earths and, of course, radium and other products of the atomic disintegration of uranium. Minerals apparently derived from pitchblende (alteration products) include: gummite (hydrous silico-uranate of Pb, Ca, etc.), soddite (hydrous uranium silicate), curite (hydrous lead uranate), becquerelite and shoepite (uranium hydroxides), kasolite (hydrous uranium lead silicate), torberite (hydrous uranium copper phosphate), autunite (hydrous uranium calcium phosphate), and carnotite, a potassium uranyl vanadate of a rather definite composition, approximating the formula $K_2O.2UO_3.V_2O_5.3H_2O$.

Historical. *Austria.*—Radium was discovered in, and first produced commercially from, pitchblende found in the silver mines at St. Joachimstal, Austria. These ores have been mined since 1517 for silver and later for cobalt and bismuth. As a result of Madame Curie's discovery and isolation of radium from these ores, the Austrian Government established a plant in 1898, which has continued production under the Czechoslovakian and German governments.

The ore is in mica schist interbedded with limestone with post-mineralization intrusions of gneiss. The veins occur as stringers and pockets 6 to 36 in. wide, containing a number of metals such as Ag, Ni, Co, Bi, As, and U in a variety of minerals. Galenite, blende, pyrite, marcasite, and cuprite occur in minor quantities. Similar but less important deposits occur in Saxony.

Portugal.—Portugal was the second nation to produce radium ores. Production has been small but consistent from autunite ores located between Guarda and Sabugal. The deposits are excellently described by Segaud and Humery.[2]

Cornwall.—Pitchblende also has been found in the tin-producing region of Cornwall, England. It occurs in veins of silver-nickel-cobalt ores where they contact dolomite. The mines are worked principally for bismuth, ocher, cobalt, and nickel. Pitchblende, being a valuable by-product, has been recovered consistently in relatively small quantities.[3]

United States.—Small and intermittent production of pitchblende has come from mines near Central City, Gilpin County, Colorado. These originally were worked for gold. The rock containing pitchblende, galena, sphalerite, etc., is a fine-grained aplitic granite. Specimens of pitchblende also have been found in feldspar quarries

[1] Engineer in charge, U.S. Bureau of Mines Experiment Station, Pullman, Wash.

[2] Segaud and Humery, Les Gisements d'uranium du Portugal, *Ann. mines, Mémoires*, Ser. 11 Vol. 3, pp. 111–118, 1913.

[3] Ussher, Barrow, and McAllister, The Geology of the County around Boduin and St. Austel, *Mem. Geol. Survey England and Wales*, 1909.

in Connecticut and pegmatite veins in North Carolina, South Carolina, Texas, and South Dakota.

But the first large-scale production of radium was derived from extensive carnotite deposits located in the arid regions on both sides of the Colorado-Utah border. These ores were discovered in 1881, but their nature was unknown until 1887. Previous to 1910, considerable carnotite was exported to Europe for treatment, and a few small local plants extracted uranium and vanadium, but no radium, with only moderate success.

In the fall of 1912, representatives of the U.S. Bureau of Mines made a survey of the carnotite deposits and announced[1] that they constituted by far the largest known source of radium ore. This bureau also made a study of methods for recovering radium, vanadium, and uranium from these ores and operated a pilot plant to demonstrate the economic possibilities of a selected process.[2] From 1916 to 1923, domestic production of radium from these deposits far exceeded the supply from all other sources.

Carnotite is a secondary mineral, canary yellow in color. It occurs as disseminated grains and incrustations in a light-colored sandstone, overlaid in places by shale and conglomerate. The deposits are erratically distributed in pockets, and the cost of mining and development is therefore high. Exceptional claims have produced 500 tons of shipping ore, which averaged only 5 to 10 mg. of radium per ton. In contrast to pitchblende, a high-grade concentrate cannot be obtained by ore-dressing processes. Lack of water and other industrial facilities in the region in which the deposits are located made it necessary to ship the ore considerable distances to reduction plants. The Bureau of Mines reported operating costs for its pilot plant in Denver as $37,599 per gram of radium recovered. The ore cost $96.33 per ton delivered. Subsequent mining costs were often higher, and the nominal market price for radium obtained from carnotite was seldom less than $100,000 per gram.

Belgian Congo.—Radium ores were discovered while prospecting for copper in Katanga, Belgian Congo, on Jan. 22, 1913. Little was done with this discovery until 1921 when active research and development was started. The deposits are in veins of moderate thickness and are extremely irregular. Primary pitchblende found in the central part of the ore bodies is surrounded by alteration products, chiefly torbernite, curite, and kasolite. The ore is of such exceptional grade that it is feasible to ship it to Belgium for treatment.

A treatment plant was established at Oolen, in the Antwerp Campine, by Union Minière and began operations in July, 1922. Because of the high radium content of the ores (100 to 150 mg. per ton) sufficient radium to supply all demands was produced at such a low cost that it soon dominated the market. The price, first fixed at $70,000 per gram, was reduced to $50,000 in 1930.

Canada.—Another rich deposit of pitchblende, discovered in 1930 on the shore of Great Bear Lake, N.W. Territories, Canada, has been developed into an important source of radium[3] by Eldorado Gold Mines Ltd. The ore is complex and of two gen-

[1] MOORE, and KITHIL, A Preliminary Report on Uranium, Radium and Vanadium, *U.S. Bureau Mines Bull.* 70, 1913.

[2] PARSONS, MOORE, LIND and SCHAEFER, Extraction and Recovery of Radium, Uranium and Vanadium from Carnotite, *U.S. Bur. Mines Bull.* 104, 1916.

[3] POCHON, Radium from the Canadian Arctic, *Eng. Mining Jour.*, Vol. 138, pp. 39–41, September, 1937.

PARMLEE, Radium from the Arctic, *Eng. Mining Jour.*, Vol. 139, pp. 31–35, April, 1938.

SMITH, Milling Pitchblende-silver Ores at Eldorado Plant, *Eng. Min. Jour.*, Vol. 193, pp. 35–38, April, 1938.

POCHON, Radium Recovery, Canada's Unique Chemical Industry, *Chem. & Met. Eng.*, Vol. 44, pp. 362–365, July, 1937.

The Staff, Eldorado Operation, *Can. Min. Met. Bull.*, February, 1938. Radium Recovery at Port Hope, *Can. Chem. Met.*, June, 1937, p. 211.

eral types, one having a highly siliceous gangue, and the other dolomitic. The latter is chiefly remarkable for its high silver content, which runs 300 to 360 oz. per ton. Crude ore is concentrated by jigs, tables, and flotation machines at the mine, and the concentrates are shipped to a plant at Port Hope, Ontario (4000 miles from the mine), where radium, uranium, and silver are extracted.

The large output of radium from this new source affected the market so that radium sold at $20,000 per gram in 1937. In 1939, a marketing agreement with Union Minière stabilized the price at $27,500. The total production of radium from all sources probably has exceeded 1 kg. Low-grade pitchblende ores have been found in pegmatite veins of Quebec and Ontario, but these have not been exploited.[1]

Australia.—Uranium ores are found in South Australia.[2] The Radium Hill Co., with works at Sydney, has treated autunite from this source.

Other Sources.—Little information is available concerning uranium ores in Madagascar, South Africa, and Russia, but there has been minor production from these sources, mostly from Madagascar.

The Nature of Radium.—Radium is the most important of a series of products resulting from the atomic disintegration of uranium. Such changes reach an equilibrium during geologic periods of time by which a maximum ratio of 1 part of radium to nearly 3 million parts of uranium is established. This equilibrium has been attained in most uranium minerals. For example, 130 mg. of radium is usually found in a ton of pitchblende ore containing 50 per cent U_3O_8.

Radium is the heaviest of the alkaline-earth group of elements, and it is so similar to barium in its chemical and physical properties that the two elements can be separated from each other only by virtue of the difference in solubility of their salts.

The amount of radium in an ore is so small that it is not possible to make a direct separation of a substantially pure radium compound. The radium must be "collected" with a barium salt, and 400,000 to 1,000,000 parts of barium to 1 of radium is required for that purpose. In all methods used to recover radium from an ore, radium and barium are brought into solution as chloride salts and then precipitated as sulphates by adding sulphuric acid (or sodium sulphate) to a slightly acid solution of radium and barium chlorides. Usually the volume of solution is so large that even the slight solubility of radium sulphate is not exceeded. Nevertheless, the radium always is precipitated more completely than the barium.[3]

This remarkable phenomenon has evoked much speculation, and for lack of a rational explanation it was referred to by Dr. S. C. Lind as pseudoisotopy. It was generally believed that adsorption played a major part in this phenomenon. However, an extensive quantitative study revealed that the behavior follows the general laws of mass action in a range of dilution that was noted for the first time in this case only because the radioactive properties made quantitative measurements possible. This investigation demonstrated that the coprecipitation of radium with barium sulphate was not due to adsorption but was the result of the replacement of barium by radium in the crystal lattice of the barium sulphate.[4]

This same phenomenon occurs when soluble salts of radium and barium, such as the chloride or bromide, are crystallized from a solution. In every case the crystal fraction will have a higher ratio of radium to barium than has the mother liquor, no matter how low the concentration of radium may be. The enrichment factor may

[1] Spencer and Carnochan, The Wilberforce Radium Occurrence, *Can. Min. Met. Bull.*, 1930.

[2] Brown, Occurrence of Uranium Ores and Other Rare Minerals Near Mt. Paniter, South Australia, *South Australia Mines Department*, 1911.

[3] Lind, Underwood and Whittmore, The Solubility of Pure Radium Sulphate, *Jour. Am. Chem. Soc.*, Vol. 40, pp. 465–472, March, 1918.

[4] Doerner and Hoskins, Coprecipitation of Radium and Barium Sulphates, *Jour. Am. Chem. Soc.*, Vol. 47, May, 1925.

be expressed by a constant that represents an equilibrium between the ratio of radium to barium in the solution and the ratio of radium to barium on the surface of the solid phase.

$$\frac{\text{Ra (in solution)}}{\text{Ba (in solution)}} \quad K \frac{\text{Ra (solid phase)}}{\text{Ba (solid phase)}}$$

This equation is merely a statement of the law of mass action in which K is the ratio of the solution pressures of radium and barium on the surface of a mixed crystal. Since K is greater than unity ($K = 1.8$ for the sulphate), the radium is more concentrated in the salt than in the solution. The important point, not generally realized, is that K is independent of the solubility of either salt alone, and the equation applies even at ratios of one to a million.

By the application of this law, radium is first separated from other ore constituents and collected with barium, and then, by a series of fractional crystallizations, it is separated from the barium. A net recovery of over 90 per cent of the radium from an ore containing only 5 mg. radium per ton is not unusual. The recovery and isolation of radium from an ore by any other means would be enormously more difficult, if not impossible.

Treatment of Pitchblende.—Methods in general use for treating pitchblende ore follow the general pattern of the process devised by Debierne and Curie for the Austrian ores. Pulverized ore was fused with sodium sulphate to convert the uranium into sodium uranate. The fused product was leached with water to remove soluble salts and then treated with dilute sulphuric acid to extract uranium sulphate. An excess of sodium carbonate was added to the hot solution to precipitate iron and other impurities which were removed by filtration. The filtrate containing soluble uranyl carbonate was acidified and boiled to remove CO_2. Then sodium uranate was precipitated by caustic soda.

Radium and barium sulphates remained in the residue from the acid leach, which consisted largely of silica, lead sulphate, etc. This residue was boiled with a solution of soda ash which converted a large part of the radium and barium sulphates into carbonates. The insoluble product was thoroughly washed to remove sodium sulphate and then treated with dilute hydrochloric acid to extract soluble radium and barium chlorides. The process of boiling with sodium carbonate and leaching was repeated several times to obtain a high extraction of the radium. Final residues from this treatment are chiefly silica containing insufficient radium to justify further extractions. A concentrate of radium-barium sulphate was precipitated from the combined acid extracts by the addition of small amounts of barium chloride and sodium sulphate. The solution, separated from the precipitate by settling, decantation, and filtration, was discarded.

The radium concentrate was again converted to a chloride solution by repeated treatment with sodium carbonate, washing and leaching with hydrochloric acid This final solution contained about one part of radium to one million of barium. By a long series of fractional crystallizations, most of the radium was separated from the barium.

In a later modification of the process, the ore is roasted with sodium carbonate and sodium nitrate. This converts the radium to a carbonate, and after thorough washing to remove soluble salts (particularly sulphates which would precipitate radium) the calcine is treated with hydrochloric acid to extract radium chloride.

Canadian ores contained so much lead, silver, and sulphides of iron, copper, etc. that other modifications of the Curie process have been necessary.[1] Mill concen-

[1] Pochon, Radium Recovery at Port Hope, *Chem. & Met. Eng.*, Vol. 44, 1937.

trates, crushed to ¼ in., are roasted at 1100°F. The calcine is mixed with 5 to 10 per cent of common salt and again roasted in a hand-rabbled furnace at a low temperature to avoid loss of silver chloride by volatilization. It is then leached with dilute sulphuric acid (with additions of $NaNO_3$, $BaCl_2$, and HCl) to extract uranium, iron, copper, etc. Sodium uranate is recovered as previously described and is purified to meet market requirements.

Residues from the acid leach are first treated with a hyposulphite solution to extract silver, which is recovered by precipitation with sodium sulphide. Lead is then extracted with boiling caustic (brine seems preferable). Extraction and recovery of radium follows the Curie method except that autoclaves are used for the soda treatment. This accomplishes more rapid carbonation than boiling at normal pressure.

Details of the treatment of Belgian ores have not been published. It has been stated that they are leached directly with sulphuric acid. Extraction and recovery of radium is carried out substantially as described above.

Treatment of Carnotite.—Carnotite is a yellow earthy mineral, occurring as a crystalline powder dispersed in sandstone. It is much softer than the sand grains to which it is more or less firmly cemented. The ore is easily crushed to the size of the sand grains (about 20 mesh), and the valuable minerals can be concentrated by attrition in impact mills followed by hydraulic or air classification. The slime or dust concentrate contains 50 to 80 per cent of the radium with a concentration ratio of 3:1 or 4:1. Subsequent recovery of radium from such a concentrate is even more difficult than from the original ore, and other methods of concentration are still less effective. Therefore concentration is limited, in general, to low-grade ores that cannot otherwise justify the cost of transportation.

The mineral carnotite, which contains vanadium as well as uranium, is commonly associated with roscoelite, a vanadium silicate. These two minerals occur in various proportions, and there is no sharp distinction between the carnotite and roscoelite ores. These ores were treated for vanadium (and uranium) before their value as a source of radium was recognized. Later vanadium was considered a by-product from the relatively more important production of radium. After several years of neglect, they are being treated again for vanadium and uranium, with a limited production of radium as a by-product that scarcely yields a profit at current prices.

There are two general methods by which radium is obtained from carnotite ores: (1) Direct dissolution of the radium from the ore by an acid, with or without a preliminary treatment to improve the extraction. (2) Concentration in a slime: A sulphating treatment, either digestion with hot sulphuric acid or fusion with sodium sulphate or bisulphate, is followed by leaching and washing to remove a solution carrying suspended slime from the barren sand. The solution, which contains soluble sulphates of uranium, vanadium, iron, and aluminum, is then separated from the suspended solids by sedimentation and filtration. The siliceous slime contains radium and barium sulphates which may be concentrated further by caustic fusion and leaching to extract silica. In any case, the radium is converted to a carbonate and extracted with hydrochloric acid.

Nitric Acid Process.—This process was originated by the U. S. Bureau of Mines and thoroughly demonstrated during the production of over 7 g. of radium in the plant of the National Radium Institute. Even though this process was not subsequently used, it led to the development of similar processes having many of the same features. For this reason and because complete data are available, this process is described in detail.

A 320-lb. charge of pulverized ore is slowly added to 320 lb. of 38 per cent hot nitric acid in stoneware pots. It is heated with live steam and stirred 15 min., then

run to stoneware vacuum filters having asbestos filter cloth. The residue is given one wash with weak acid and two with hot distilled water.

The large amount of acid is necessary to react with the acid-soluble ore constituents such as the compounds of iron, uranium, vanadium, aluminum, and calcium and leave a sufficient excess to hold the radium and barium in solution. Only ores containing relatively small amounts of sulphates, organic matter, and vanadium give satisfactory results when treated by this method. Sulphates reduce the extraction of radium by precipitating the slightly soluble radium sulphate. Organic matter causes excessive frothing, consumes acid, and slows up filtration. If the ore is rich in vanadium, a slimy precipitate of vanadic acid clogs the filter. Slow filtration allows the charge to cool, which causes precipitation of various salts, including radium. Concentrates are especially difficult to treat because they contain a high proportion of soluble constituents and the slimy charge filters with great difficulty.

On suitable ores, however, the nitric acid leach extracts over 90 per cent of the radium, which is considerably better than is usually obtained by other direct leaching methods. The residue from the acid treatment may contain considerable vanadium, most of which can be readily extracted by an alkaline leach and recovered.

Precipitation of Radium.—The acid solution (filtrate) is run into a large redwood precipitating tank, where it is diluted with water and neutralized with a solution of caustic soda. If too much alkali is added, iron and vanadium precipitate and contaminate the radium product obtained later. On the other hand, insufficient alkali leaves the acidity too high, and the solvent action of the acid prevents complete precipitation of the radium. A solution of barium chloride is next added (about 2 lb. $BaCl_2$ to 1 ton of ore) sufficient to make the ratio of barium to radium about 1 million:1. After mixing the solution, sulphuric acid (about 15 lb. to 1 ton of ore) is slowly added with continued stirring. After stirring an hour the whole solution, containing radium-barium sulphate in suspension, is pumped to a settling tank having a conical bottom. The sulphates are allowed to settle 4 days, and then, after siphoning off most of the clear solution, they are run to a small earthenware filter and washed.

Separation of Radium from Barium.—The radium-barium sulphate thus obtained is of an excellent purity, often as high as 90 per cent. It is converted to an acid-soluble sulphide by reduction with charcoal. A mixture of the sulphate with one-fifth its weight of charcoal is heated 8 hr. in a graphite crucible at about 800°C. The calcine is leached with pure dilute hydrochloric acid, care being necessary to remove the dangerous gas, hydrogen sulphide, which is generated. Most of the radium and barium are obtained in the solution as chlorides, and the radium is concentrated by crystallization, as previously described. The small residue filtered off from the chloride solution is given a second reduction and leach to extract the residual radium.

This procedure replaced the slow and more costly method by which the sulphates are converted to carbonates by repeated digestion with a solution of sodium carbonate.

Precipitation of Iron, Calcium, and Aluminum.—The solution from which the radium was first precipitated is run into a tank containing an excess of sodium carbonate in a boiling solution. Iron, calcium, and aluminum are precipitated, also some of the vanadium. In order to prevent an excessive loss of vanadium and uranium in the precipitate, it is necessary to have a considerable excess of sodium carbonate in the solution at all times, the liquor must be added slowly, and the mixture must be kept boiling hot and agitated during and for several hours after the addition. About 650 lb. of soda ash to 1 ton of ore is required, and it takes about 6 hr. to complete the operation. The iron precipitate is filtered off and discarded. Although it contains about one-fourth of the vanadium present in the acid solution, re-treatment of this residue to recover the vanadium is not profitable.

Precipitation of Uranium.—The filtrate from the iron precipitate, containing uranium and vanadium, is run to another tank where it is partly neutralized with nitric acid. After stirring with air, sodium hydroxide is added to the hot liquor until uranium is completely precipitated as sodium uranate. The solution is boiled for 1 hr. and then filtered through a press. The uranium precipitate is washed in the press, then removed and dried. It contains about 8 per cent vanadium oxide and must be refined to make a marketable product. About 85 per cent of the uranium is recovered.

Precipitation of Vanadium.—The filtrate from the sodium uranate is run to another tank, neutralized with nitric acid, and boiled to remove carbon dioxide. A solution of ferrous sulphate is then slowly run into the hot liquor, which is agitated with compressed air. The vanadium precipitates as ferrous vanadate. It requires considerable care and experience to obtain a complete recovery of the vanadium and at the same time produce a product of acceptable grade, *i.e.*, over 32 per cent vanadium oxide. The precipitate is filtered off in a press, washed, and dried. The vanadium recovered, including that obtained from the sodium uranate, averages only 30 per cent of that in the ore.

The filtrate from the ferrous vanadate is almost wholly a solution of sodium nitrate. It is evaporated in iron tanks heated by steam. Air is blown into the solution to aid evaporation. When sufficiently concentrated, the liquor is run into shallow steel pans where sodium nitrate crystals form. These are collected and used to make nitric acid for the leaching operation. As the losses of nitrate are small, the acid cost is less than that of an equivalent amount of hydrochloric acid.

Although the nitric acid process recovered the radium effectively, recovery of vanadium was poor. The relative values of radium and vanadium made a high recovery of radium the chief consideration, but it soon became apparent that the recovery of vanadium is equally important. This led to the use of other methods and also to improvements in the nitric acid process.[1]

Preliminary Roast.—Carbonaceous material found in nearly all carnotite ores causes frothing and excessive consumption of acid when leached with hot nitric acid, and many highly carbonaceous ores are not amenable to direct acid treatment. A preliminary roast at 700°C. with excess air removes the carbonaceous matter and converts the iron to a less soluble condition. After roasting, less iron and more of the radium is extracted with less acid and the pulp is much more easily filtered. This is very important when treating dust concentrates.

Alkaline Leach.—Carnotite ores were first treated to extract uranium and vanadium by boiling with a solution of sodium carbonate, and no effort was made to recover radium.[2]

This step not only extracts vanadium and uranium, but it converts acid-soluble sulphates (such as gypsum) to carbonates and water-soluble sulphates, which are separated from the residues with the vanadium and uranium. This prevents reprecipitation of radium when the latter is subsequently extracted with acid.[3] Moreover, after calcination and an alkaline leach, dilute nitric acid at 50°C. gives a better extraction than can be obtained from the crude ore with boiling hot strong acid.

Improved Nitric Acid Process.—The crushed ore is first roasted at 700°C. It is then fed into a rod or pebble mill with water and one-fourth its weight of soda ash.

[1] DOERNER, Notes on the Extraction and Recovery of Radium, Vanadium and Uranium from Carnotite, *U.S. Bur. Mines Repts. Investigations* 2873, 1928.

[2] Haynes-Engle, U. S. patent 808839.

[3] One firm used an autoclave for the alkaline treatment (W. F. Blecker, U. S. patent 1438357). If caustic soda is added with the soda ash, then vanadium is extracted and sodium uranate remains in the residue to be extracted with the radium by the acid treatment.

After thorough disintegration and digestion in the hot solution, the pulp is filtered and washed with hot sulphate-free water. The filtrate is used subsequently to neutralize the acid solution, so this alkaline leach does not involve any extra cost for chemicals.

Recovery of Radium.—Dilute nitric acid (1 part to 4) at 50°C. may be used to extract the radium and also any uranium and vanadium not extracted by the previous step. A digestion period of several hours is required, and the addition of a little sodium fluoride improves the solvent action. Filtration and washing are easy and rapid. Radium-barium sulphate is precipitated and recovered from the combined alkaline and acid solutions by the usual methods.

Recovery of Uranium and Vanadium.—After filtering off the radium-barium sulphates, the filtrate is made slightly alkaline and heated to precipitate vanadium and uranium. Addition of only a little ferrous sulphate is required to complete the precipitation. After stirring for an hour or more the precipitate is filtered but not washed. Sodium nitrate is recovered from the filtrate.

The uranium-vanadium precipitate is dried and then fused with two parts, by weight, of sodium sulphate containing a small proportion of nitrate or caustic. The vanadium is leached from the crushed slag with hot water and then precipitated as high-grade vanadic acid by boiling the acidified ($\frac{1}{25}N$) solution.

Uranium is dissolved from the residue of the vanadium extraction with warm dilute sulphuric acid. Iron and other impurities are then precipitated with sodium carbonate and removed by filtration. After neutralizing the filtrate with sulphuric acid and boiling off CO_2, sodium uranate is precipitated with caustic soda, filtered off, and washed.

Hydrochloric Acid Leach.—Hydrochloric acid is even less effective than nitric acid for extracting radium from ores containing sulphates, but it is much better for extracting the vanadium. This acid is quite satisfactory for the treatment of selected ores and has been widely used in processes that follow the general procedure described for nitric acid except that the sodium salts are not recovered and treated to regenerate the acid. It also has been used to treat Cornish pitchblende and Portuguese autunite, but it is not applicable to most pitchblendes.

Sulphuric Acid Leach.—Hot concentrated sulphuric acid will extract radium from an ore or concentrate, and radium sulphate is precipitated from the acid solution by dilution with water. Attempts to use this method have failed on account of the high cost for acid and the difficulties encountered in the handling and filtration of hot concentrated acid.

Sliming Methods.—A sulphating treatment followed by a mechanical separation of the slime from the sand has been used to obtain a low-grade radium concentrate. The basic constituents of the ore are first converted to sulphate by one of the following treatments:

1. Fusing with sodium acid sulphate.
2. Baking with concentrated sulphuric acid.
3. Digesting with dilute sulphuric acid (sometimes HCl is also used).
4. Aerating a suspension of the ore in hot water with a mixture of sulphur dioxide and air.

The hot sulphated product of 1 or 2 is dumped into a tank of water and agitated to dissolve the soluble salts. In all cases a barren-sand residue is separated by hydraulic classification. This is usually done by decantation, using a siphon to draw off the slime from the quickly settling sand. The latter is washed clean by several decantations with water. After the decanted slime has settled for several days in large tanks, most of the clear solution is siphoned off and the rest is separated by filtration.

Three products are thus obtained: a barren-sand reject, a slime concentrate containing at least 90 per cent of the radium, and an acid solution from which vanadium and uranium are recovered by the methods previously described.

Several treatments with a hot solution of sodium carbonate, each followed by thorough washing and an acid leach, are required to extract radium from the siliceous slime. This treatment is often preceded by a fusion with caustic soda and a leach to remove most of the silica as a water-soluble silicate. A high-grade radium-barium sulphate is precipitated from the acid extract and treated for the recovery of radium by the standard methods previously described.

Refining Radium.—When half the salt is crystallized from an acidified solution of radium and barium chlorides, approximately 80 per cent of the radium will be concentrated in the crystallized fraction. Hence the concentrations of radium in the crystals and mother liquor will be, respectively, 1.6 and 0.4 times the concentration of the original solution. If the process is repeated with both fractions, four products are obtained having concentrations of 0.16, 0.64, 0.64, and 2.56 with respect to the original solution. Now, combining the two middle fractions (crystals from the first mother liquor and liquor from the first crystals), the next fractionation yields six products with the following relative concentrations: 0.064, 0.256, 0.256, 1.02, 1.02, 4.10.

By thus combining fractions of equal concentration and adding fresh liquor to fractions approximating its own concentrations (in this case the 1.02 fractions) this process can be extended indefinitely to yield any degree of concentration required. The next step will yield end products having the relative concentrations of 0.027 on the minus, or liquor, side and 6.56 on the plus, or crystal, side.

Since the quantity of material treated decreases rapidly in both directions, it is convenient to establish several separate series in which each system is supplied from the end crystals of the preceding series. Each series will have 8 to 12 steps.

A solution of radium and barium chlorides having a ratio of 1 to 3 parts of radium to a million of barium is finally obtained by all methods of recovering radium. The first crystallizing series is carried out in steam-jacketed vessels of 30 to 100 gal. capacity, usually eight or nine in number. These vessels must have an acid-proof lining because the solutions contain free acid.

The largest, or zero, pot at the center of the series is filled with fresh solution and evaporated until a cool draft of air will cause crystals to form on the surface. Cold water is then passed through the steam jacket, and about half the salt will crystallize overnight. The mother liquor is siphoned into a smaller -1 pot, and the crystals are transferred to a $+1$ pot in the opposite direction.

The crystals are dissolved in dilute acid, and a half fraction is recrystallized. At the same time, another crop of crystals is obtained in the -1 pot. Mother liquor from the -1 pot is siphoned to a -2 pot for another fractionation, and the crystals, transferred to the 0 pot, are combined with liquor from the $+1$ pot and fresh solution. In this manner the crystals progress in a $+$ direction and the mother liquors in the opposite direction, four steps each way in a continuous cycle of operations.

Mother liquor from the -4 pot carries only 25 to 30 parts of radium to one billion parts of barium. It contains most of the barium and only 1 or 2 per cent of the radium that enters the system. Part of this liquor is used to supply barium salt to the plant solutions, and the rest is discarded.

Crystals from the $+4$ pot will carry most of the radium at a concentration nearly seven times that of the original solution. They are treated in a second series of fractional crystallization carried out in porcelain dishes heated over gas burners, and the procedure is similar to the first series but can be carried out much faster in the

smaller containers. Mother liquor from the minus end of this series is returned to the first series.

Removal of Lead.—The chloride crystals on the plus side of the second series are dissolved in water without acid, and placed in a large glass precipitating jar 16 or 18 in. high. Make ammoniacal and pass in hydrogen sulphide until the precipitation of lead as lead sulphide is complete. This sulphide is filtered and collected and may be analyzed for its radium content. It should be stored for recovery of the radium by fusion with sodium carbonate. Attempts to precipitate the lead as sulphide even from slightly acid solution usually result in obtaining a brick-red precipitate of the formula $(PbS)_x.PbCl_2$ which is far more soluble in acid than lead sulphide; hence, complete precipitation of the lead is possible only in ammoniacal solution. If the solution is made alkaline with ammonia before passing in the hydrogen sulphide, only a small amount of radium is precipitated with the lead, usually not more than 0.2 per cent.

Conversion to Bromide.—Into the filtrate from the lead precipitate, powdered ammonium carbonate is introduced gradually with vigorous stirring until all the barium has been precipitated as carbonate. After standing overnight for the settling of the barium carbonate and the thorough precipitation of the radium carbonate, the supernatant solution is siphoned off as far as possible and the rest is thrown on a Büchner funnel, where it is filtered and washed several times with distilled water. The filtrate, which carries only small traces of radium, is stored and may be returned to the plant at some convenient point before the precipitation of the radium. The amount of radium in the liquor is surprisingly low, usually 0.001 to 0.003 mg. per l. The barium-radium carbonate is removed from the Büchner funnel and is dissolved in chemically pure hydrobromic acid of 20 to 35 per cent strength in a large glass precipitating jar.

Fractional crystallization is now continued in silica vessels in fairly strong hydrobromic acid solution in which the separation factor is considerably higher than in the chloride system. Concentration, therefore, takes place more rapidly, but greater care in handling the vessels is, of course, necessary on account of the higher radium concentration. Heating may be carried on on tripods with bare gas flames until the richer fractions are reached, when the evaporation is carried out on an electrically heated water bath in which only distilled water is used. In case of an accidental loss of radium solution into the bath, all the water can be drawn off and returned into the system just before the treatment with hydrogen sulphide.

The evaporation required to obtain a suitable batch of crystals may be generally regulated by concentrating the solution until vigorous fanning just begins to cause the formation of crystals on the surface of the hot solution. Of course, the higher the acid concentration, the more generous the crystal batch will be, and it is usually convenient to have the acid concentration such that about half of the barium in solution will crystallize out. Owing to the high factor of enrichment as bromide, the radium content of the mother liquor from the "minus two" bromide vessel is extremely low. In general, the amount of radium returned to the plant in this bromide mother liquor is only about 0.2 per cent of the total amount going through the system. If such a result is actually obtained, it is more convenient and economical to use the bromide mother liquor for the recovery of hydrobromic acid than to return the mother liquor to the plant to recover its small radium content.

Number of Fractions Employed.—The number of fractions employed in the plus direction in the bromide system varies with conditions, 10 to 12 being the usual number. The crystallization is conducted in such a way that the radium bromide collected in the final fraction should not fall below 1 per cent of barium bromide, and sometimes is as high as 3 or 4 per cent. The total weight of the fraction should be 1 to 2 g. This fraction, after thorough drying in a hot-air oven, is sealed in a glass tube and kept for

final purification, when a sufficient number of tubes have been accumulated. The amount of radium in the tube can be easily determined by means of the gamma-ray method, to be described later. After 20 or 30 tubes have accumulated, they are opened and the contents dissolved in hydrobromic acid in a small silica dish.

If there is any considerable difference in the activity of the salt in the different tubes, it is wiser to put those together which have approximately the same activity for the initial solution, and to put those of higher activity in a +1, +2, or +3 dish, depending on the amount of radium present. Crystallization is then continued with a general tendency to push up the radium from the lower fractions into the last silica dish in which the majority of the radium is finally accumulated. After thorough drying in a hot-air oven to free the salt from moisture and from water of crystallization, it is placed in a glass tube and hermetically sealed. In this tube a small platinum wire is sealed through one end in order to conduct away the unipolar charge that may collect in the interior, attaining voltages that could cause destructive sparking. Reports are on record of serious radium losses having resulted through neglect of this precaution.

RADIUM MEASUREMENTS

Measuring Instruments.—The methods used for determining the amount of radium either in an ore or in a product such as a concentrate containing radium depend entirely upon the fact that radium and other radioactive substances ionize gases. Such ionization is due to the alpha, beta, and gamma rays which are emitted by radioactive substances. The methods are, therefore, entirely physical in character and involve any means of recognizing qualitatively or quantitatively the ionization in air or other gases produced by the alpha, beta, and gamma rays. Two instruments are usually employed for such a purpose, *viz.*, an electrometer or an electroscope.

The first instrument is adapted for use in chemical and physical laboratories, and is especially useful where a large number of readings are desired on a radioactive material in a short space of time. For example, where a decay curve is required and the points on the curve involve short intervals of time, an electrometer is very useful, as the length of time for making a reading on even a not very sensitive product is short, owing to the sensitiveness of the instrument that may be used. For ordinary practical purposes, however, an electroscope is much more satisfactory, and the use of the electroscope only will be described in detail in this article. A suitable instrument usually consists of two compartments, one above containing a suspended gold or aluminum leaf, in front of which is attached a reading microscope, and one below in which the ore, radioactive solid or radioactive gas, to be tested is placed.

If the material is a solid, there is a suitable door to the lower compartment which can be opened or closed for the introduction of the material. If radioactive gas is to be tested, the lower compartment is airtight and has two stopcocks, one for exhausting the chamber, and the other for the introduction of the gas after partial or complete exhaustion. Usually the leaf is electrically charged by a piece of vulcanite rubbed on the sleeve of a coat, or by a battery of small dry cells, or any other suitable means of getting a sufficiently high voltage; the charge causes the leaf to rise. Then the natural leak of electricity from the leaf is noted on the scale, using a stop watch to determine the time the leaf drops between two different points, and calculated as a certain number of divisions per minute.

Approximate Method for Solids.—If an approximate determination of the activity of a solid such as an ore is desired, the material is placed in the compartment below and the leak of the leaf noted as before. If the ore contains uranium-radium, or any other radioactive element, the rate at which the leaf falls will always be faster than the natural leak of the instrument itself, owing to the ionization of the air in the chamber

by the rays given off from the radioactive material. There are a number of precautions, however, to be taken in making such measurements: (1) The illumination during the taking of the readings should be constant, and therefore it is better to have the electroscope in a room artificially illuminated rather than to use ordinary daylight, which will vary from time to time. (2) Readings should always be taken between the same points on the scale. (3) In comparing two ores, their physical conditions should be as nearly as possible the same. This may be roughly assured by passing them through the same mesh sieve, preferably 40 or 60 mesh. Of course, every particle of the ore must be ground until it finally passes this sieve. The same weight should be taken, and the same surface should be exposed in the electroscope.

In order to get these conditions conveniently, it is advisable to use a brass plate about ¼ in. thick, of a size to fit into the bottom compartment of the electroscope; and in this should be cut, by means of a lathe, a circular depression ⅛ in. deep and about 3 in. in diameter. This can be done by any brass worker. The bottom and the sides of the depression should be perfectly smooth. The ore to be tested is poured into the depression, the plate tapped gently so as to settle the ore, and then, by passing the edge of a flat piece of metal across the surface of the plate, the extra ore is wiped off and the depression left exactly filled with ore, having a flat surface. In this manner a fairly uniform weight of material is obtained for comparison, and the surface exposed in the electroscope is approximately constant. Of course, the density of the ores tested varies, but the method gives approximate results. The plate with the ore is introduced into the bottom compartment of the electroscope and a reading taken. The ore is removed and replaced by a sample of carnotite of known uranium content, which serves as a standard. This sample, of course, is passed through the same mesh sieve as the sample being tested. The relative radioactivities, *i.e.*, the rates at which the leaf falls, are roughly proportional to the amount of radioactive elements present.

With an ore, the total activity will be due to the uranium, radium, and other disintegration products of the series. With a concentrate, such as radium-barium sulphate, the activity will be due to radium alone. Too much emphasis cannot be placed upon the fact that this method can be used only to compare similar radioactive products, and results are only approximate. For example, a carnotite ore must be checked against an analyzed carnotite ore, pitchblende against an analyzed pitchblende ore, and a concentrate against a similar type concentrate. As has already been pointed out, the physical condition of the material affects the results very markedly.

The following example will show how to make a calculation:

Natural leak of instrument = 5 divisions in 10 min.

Natural leak of instrument = 0.5 division per minute.

Rate of fall of leaf with standard ore (3 per cent U_3O_8) = 48.5 divisions per minute.

Rate of fall of leaf with ore to be tested = 36.5 divisions per minute.

Subtracting from each of these figures the natural leak, 0.5 division per minute, the results are 48 and 36. The percentage of U_3O_8 in the ore will then be $(36 \times 3)/48 = 2.2$.

If the natural leak is as low as 0.5 division per minute and the radioactivities of the samples are as high as those indicated in the above experiment, the natural leak can be neglected, as the error from it is less than the probable experimental error.

Exact Determinations by Emanation Method.—The exact determination of radium is done by means of the emanation method, which involves separating radium emanation as a gas from its parent radium, and measuring its quantity in a gastight electroscope previously standardized with a known amount of radium emanation. Analyzed pitchblende has been employed to furnish known quantities of emanation for purpose of standardization. Pitchblende is selected because it is a primary

uranuim mineral and contains the equilibrium amount of radium to uranium. Therefore, by analyzing the mineral carefully for uranium it is possible to calculate exactly the amount of radium present; and a satisfactory standard is thus readily obtained. Secondary uranium minerals, such as carnotite, autunite, torbernite, etc., do not always contain the equilibrium amount of radium and, therefore, cannot be used as a standard.

Three general methods of procedure may be used, as follows: (1) Release and measure the emanation from a substance in which it is in equilibrium with the radium content. This condition will usually not be fulfilled unless the substance has been retained for a month or more in a closed container. In exceptional instances, however, the radium might be contained in a solid of very compact structure, or with a glazed surface, so that no spontaneous loss of emanation could take place. But even with a dense mineral like pitchblende, the leak of emanation, called "emanating power," amounts at ordinary temperature to several per cent.

This circumstance suggests the second procedure: (2) Liberate and measure the emanation retained in the solid and apply as correction the "emanating power," which must be determined separately and preferably after the solid has been in a closed retainer for a month. Both of the above procedures, applicable, in general, to solids only, involve in practice long delays; and, although they are adapted to scientific investigation, they are not suited to radium measurements for the purpose of plant control when quick results are desired.

The following procedure is shorter and preferable when its use is possible: (3) Remove the emanation completely from the sample of the substance to be analyzed for radium; close it at once in a gastight vessel and allow the emanation to accumulate for a convenient period, such as 1 to 10 days. Then remove it and measure it, making a time correction to find the maximum amount that would have been formed on the attainment of equilibrium. For removal of emanation the radium must be contained either in solution, or in a state of fusion. When radium and barium are in a solution together, and there is a tendency for partial precipitation, either as a sulphate or as a silicate, the two elements will usually precipitate in the proportion in which they exist in the solution. The presence, therefore, of a moderate amount of barium in solution has a tendency to hold the radium in solution and to give more exact results by the emanation method.

Treatment for Solution Containing Barium in Large Excess over Radium.—For a solution containing barium in large excess over radium, the treatment is as follows: Place a suitable portion of the solution—such as will contain about 1×10^{-8} g. of radium—in a small Jena flask and add to it a suitable quantity of 1:1 nitric acid. Add a few glass beads and boil 5 to 10 min. to remove all emanation. Allow slight cooling, and then close the flask tightly with a one-hole rubber stopper provided with a glass tube drawn out above to a capillary tip. Seal the tip while some steam is still in the flask, in order to provide a partial vacuum, which should be maintained until the flask is again opened, thus affording a proof that no outward leak of gas has taken place. Note the exact time and date of sealing.

The treatment for a solution containing little or no barium is to add a suitable portion of 1:1 nitric acid which is saturated with barium nitrate, and then proceed as in the treatment described above.

Procedure for Liquids Containing Excess of Sulphate or Carbonate.—The detailed procedure for treating a liquid containing an excess of sulphate or carbonate, but no barium, is as follows: An excess of barium salt is added to the liquid, and the precipitate is filtered off. The filtrate containing an excess of barium is made acid with nitric acid to the point of precipitation, and is given the treatment outlined above for a solution containing barium in large excess over radium. The precipitate, if barium

sulphate, is fused with four or five times its weight of fusion mixture of sodium and potassium carbonates and is treated as described later for fusions. If the precipitate is barium carbonate, it is dissolved in nitric acid containing sufficient sulphuric acid to precipitate an amount of barium sulphate convenient for fusion, which is filtered off. The filtrate that is obtained may be combined with the original filtrate and given the treatment as described for a solution containing barium in large excess over radium. All radium is then contained either in the filtrate, with an excess of barium, or in the barium sulphate precipitate. The latter is fused with sodium carbonate and treated as described in the next section. Both of the liquid fractions are closed simultaneously (within 15 min.) so that the time of accumulation will be the same for both lots of emanation which can be later introduced into one electroscope to determine the total radium.

Fusion Method for Radium Determinations.—If the radium is contained in a substance not readily soluble, such as a radium-barium sulphate, fuse a suitable quantity in a small platinum or porcelain boat with four to five times the weight of sodium or potassium carbonate and note the exact time at which the material becomes solid. Close this boat in a glass tube as shown in Fig. 1. Allow the ema-

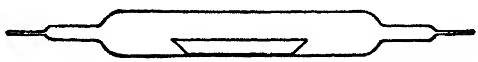

FIG. 1.—Apparatus for fusing Ra-Ba sulphate.

nation to accumulate 2 or 3 days. Connect the glass tube at one end to a highly exhausted electroscope and at the other to a stopcock. Break the glass tips inside the rubber connections and exhaust the air from the glass tube into the electroscope several times, leaving enough vacuum in the electroscope chamber to accommodate the gas to be introduced later. Break the glass tube, remove the boat and its contents, wrap in a filter paper, and place in the neck of a flask, as shown in Fig. 2; it is then ready for treatment with 1:1 nitric acid after the flask has been connected with the gas burette as shown in Fig. 3. In this treatment the flask is tipped until the acid comes in contact with the carbonate fusion, thus beginning a gas evolution. The stopcock is immediately opened to the gas burette above, and the boat and contents are then thoroughly wet with acid and jarred down from the neck of the flask to the body of the acid.

In larger fusions, the evolution of carbon dioxide may become rapid and care should be taken in handling them; but in small fusions not exceeding 1 g. the boat may be shaken down directly into the acid, which should be heated to boiling as soon as the gas evolution begins to slacken. All the carbon dioxide is, of course, absorbed by the strong sodium hydroxide solution which is contained in the gas burette. The boiling off from this point is performed as with solutions discussed below.

Boiling off Emanation from Solutions.—For boiling off emanation from solutions, the procedure is as follows: Set up an apparatus as shown in Fig. 3, wiring rubber connections at *a* and *b* to ensure tightness. Put into the leveling bulb *c* a stick of sodium hydroxide 2 to 3 in. long, or more if a large quantity of carbon dioxide is to be absorbed; make sure that stopcock *d* is closed and stopcock *e* open; pour boiling distilled water into the leveling bulb and allow the alkali to get into solution. If the boiling is too violent, put a one-hole stopper lightly into the mouth of the leveling bulb. After the alkali has gone into solution, raise the leveling bulb until the gas burette is filled to the stopcock *e*. If the quantity of air to be boiled off is small, some air may at first be left in the gas burette. Close stopcock *e*, and lower bulb *c* to its original position. Break the glass tip *f* inside the rubber tubing at *a*, and slowly open *d* to ascertain whether there is vacuum in the flask *g*. If so,

close d again and begin to heat flask g over wire gauze. Test the vacuum every few seconds, and as soon as the pressure is outward open d, and cause the flask to boil vigorously. Continue boiling until live steam has heated to boiling all the liquid in the gas burette h. This boiling should never be less than 5 min., and sometimes 10 to 15 min. of boiling is desirable. After the glass tip f has been broken, it is likely to be carried upward by steam and in some instances has lodged in the stopcock d and caused serious explosions. As a precaution, a roll of thin platinum foil can be introduced into the glass tubing, as indicated at i, or the stopcock d may have a wide bore, which also obviates the danger mentioned.

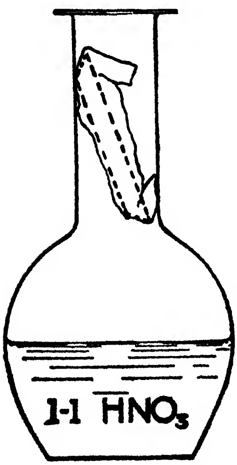

FIG. 2.—Fusion ready for acid treatment.

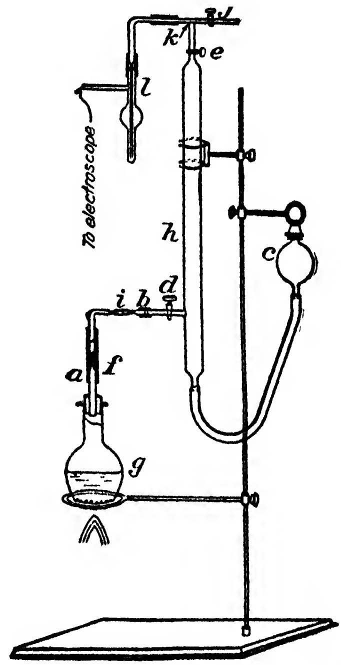

FIG. 3.—Apparatus for evolving emanation and transferring to electroscope.

After the boiling off has been completed, remove the flame, and as soon as the liquid begins to draw back through the stopcock d close the stopcock and remove the flask entirely. Evacuate the electroscope chamber to a suitable vacuum, either by an aspirator, or, more conveniently, by a hand pump, and connect the sulphuric acid microdrying bulb l to the electroscope and to the gas burette as indicated in Fig. 3. Be sure that stopcock j is closed; open first the cock of the electroscope for a moment and reclose it; then slowly open stopcock e to full width and then gradually open the stopcock to the electroscope, allowing the gas to bubble through the microdrying bulb at a fairly rapid rate.

When the liquid in the gas burette has risen exactly to the point k close stopcock e and open stopcock j, allowing dry, dust-free air, which should preferably be taken from outside the laboratory, to sweep out the connections for a few minutes; then close the stopcock to the electroscope, reopen stopcock e, and allow the liquid in the gas burette to fall back 3 or 4 in. below the shoulder; close e, and then pour off all excess

liquid out of c; close j and again open e to the electroscope, allowing air to bubble from the bottom of the gas burette h through its entire length to ensure the removal of any emanation that may have remained dissolved in the liquid. Air should be allowed to bubble into the electroscope chamber until normal pressure has been almost restored. The above procedure for boiling off radium emanation is used for carbonate fusions introduced into acid, and also in handling any solids that are to be dissolved directly. For example, ground pitchblende and carnotite ore may be wrapped in filter paper in the way in which such a fusion is wrapped in Fig. 3, or sealed in small glass bulbs which are opened by being crushed against the bottom of the flask by tapping on the glass stem projecting through a second hole in the rubber stopper.

Construction of an Electroscope.—Figure 4 shows an electroscope that is very suitable for radium determinations by the emanation method. Figure 5 represents

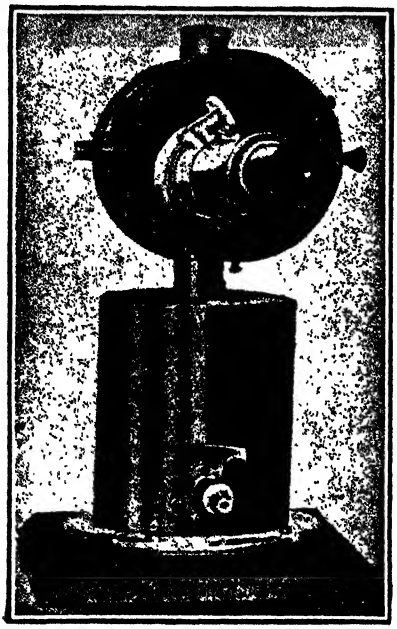

FIG. 4.—Electroscope with interchangeable ionization chamber.

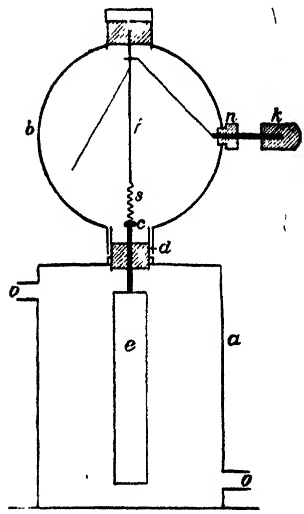

FIG. 5.—Cross section of electroscope (one-fourth size.)

a section of this electroscope, showing the gastight chamber at the bottom with openings at o for connections with stopcock. The electrode e is a brass cylinder ½ in. in diameter. It is suspended by a small brass rod ⅛ in. in diameter, which screws into the top of the electrode, passing upward through the insulating material d, and terminating in a small conical top c, serving to make metallic contact with the leaf system above. The leaf system f is supported from the top of the cylinder, where it is held in place by the sealing-wax insulation set in a milled-head cap g, which screws into a vertical collar on the cylinder ¼ in. in height. The cap is hollowed out inside to contain the insulating wax, from which a flat brass rod f, ¼ in. broad, about $\frac{1}{16}$ in. thick, and 2¼ in. long, projects downward, terminating below in a light brass spring s, to make contact with the conical top of the electrode of the ionization chamber. The leaf is of aluminum, about 2 in. in length, and is attached to a small offset at the top of the brass rod by a moisture contact. The electroscope can either be charged by a piece of hard rubber or, better, by a battery of flashlight storage cells giving 500 or

600 volts. The reading microscope in front of the instrument carries a micrometer scale serving to measure the rate of discharge of the leaf. The eyepiece fits firmly into the case so that its rotation is difficult after the micrometer scale has been set parallel to the leaf.

Order of Procedure in Using Electroscope.—(1) Set up the electroscope and charge for 15 min. from a battery with just sufficient voltage to hold the leaf on the part of the scale to be used later. (2) Observe the natural leak during 15 or more minutes. (3) Carry out the calibration control by means of penetrating rays if radium is available for this purpose. (4) Detach the top and evacuate the lower chamber to the desired vacuum. (5) Pass the emanation-air mixture through a sulphuric acid drying tube into the evacuated chamber and restore normal pressure. (6) Allow the emanation to stand in the discharge chamber for 3 hr. (7) Charge for 15 min. as before. (8) Take three readings if agreements are good, or ten if deviations are greater than 1 per cent. (9) Clean out the emanation chamber by drawing dry dust-free air through it for some time (overnight if convenient). (10) Calculate the discharge and subtract the natural leak, expressing both in divisions per second. (11) Compare the corrected discharge with the calibration of the instrument to determine the quantity of radium under measurement, taking time corrections into consideration.

Calibration of Electroscope.—The calibration of the electroscope is carried out in exactly the same way as in ordinary measurements, except that a known quantity of emanation is introduced. This known quantity may be obtained in two ways, as follows: (1) From a standard solution of some radium salt by passing air through it until its emanation is all transferred into the electroscope. This method is not satisfactory, as it is difficult to know always the amount of radium in solution, owing to the tendency of a portion of the radium to precipitate out of solution as sulphate or silicate. (2) The preferable practice is to use high-grade analyzed pitchblende, a suitable quantity being dissolved for each standardization, and the quantity of radium being calculated from the uranium analysis. The quantity of radium emanation obtained on dissolving the pitchblende will not correspond exactly to the radium content because a small fraction of 2 to 10 per cent of the gas diffuses from the ore; this fraction, termed the "emanating power" of the ore in the cold, must be determined by sealing a quantity of the ore in a tube for a month or more, and drawing off the emanation into an electroscope by the passage of air. The "emanating power" thus determined in the standard sample is used as a subtraction correction. Convenient quantities of radium emanation are those which will produce a discharge of the order of one to two scale divisions per second. The use of pitchblende as a standard is based on the fact that in any unaltered uranium mineral the ratio of the radium present to the uranium is constant. One gram of uranium is in radioactive equilibrium with 3.3×10^{-7} g. of radium.

Sample Determination of Radium Content of an Ore.—A sample of pitchblende loses 10 per cent of its emanation at room temperatures. It contains 50 per cent metallic uranium. Therefore 22 mg. of the ore will, on dissolving in acid, liberate emanation in equilibrium with 10 mg. (0.01 g.) of metallic uranium. This emanation, 3 hr. after introduction into the electroscope, causes the leaf to fall at the rate of 40.5 divisions per minute. The natural leak (0.5 division per minute) subtracted from this leaves 40 divisions per minute due to the emanation. Therefore the fall of one division per minute represents the total emanation associated with $0.01/40 = 2.5 \times 10^{-4}$ g. of uranium in the mineral. This is the "constant" for the electroscope. One gram of ore is fused with fusion mixture as already described. At the end of a month the emanation obtained from the two solutions is introduced into the electroscope. After 3 hr. the rate of fall of the leaf is 18.5 divisions per minute. Sub-

tracting the natural leak (0.5) leaves 18 divisions per minute. Therefore 1 g. of the ore contains $18 \times 2.5 \times 10^{-4} = 45 \times 10^{-4}$ g. of uranium.[1] As 1 g. of uranium is in radioactive equilibrium with 3.3×10^{-7} g. of radium, 1 g. of the mineral will contain $(45 \times 10^{-4}) \times (3.3 \times 10^{-7}) = 1.48 \times 10^{-9}$ g. of radium.

OTHER RADIOACTIVE ELEMENTS

Mesothorium.—Of the other radioactive elements that have commercial use mesothorium is the most important. It is a disintegration product of thorium and is, therefore, associated with this metal in all thorium minerals. Its half-life period is very short, compared with that of radium, being only 5½ years. Therefore, commercially it has not the same value as radium, especially for cancer treatment, or for purposes where it would naturally be carefully preserved and a long life would be of advantage. When its commercial use is likely to last over a limited period, such as in luminous paint for cheap watch dials and electric push buttons, it is just as useful as radium and can be substituted for the latter element in luminous paint for such purposes. Since mesothorium 1 gives off beta rays only, and the alpha rays are the main source of luminosity in paints used for watch dials, etc., it is necessary for the mesothorium 1 after preparation to be allowed to "ripen" for a year or even two years so that the alpha rays, due to the gradual accumulation of radiothorium, can be used. The general effect, therefore, is for the luminosity of such paints gradually to increase for two or three years and then, after coming to a maximum, gradually to decrease. Mesothorium 1 chemically is allied to barium and radium and, therefore, can be precipitated with barium just as radium is. The usual procedure in manufacture is to add 2 or 3 lb. of barium chloride per ton of monazite treated. When the monazite is heated with sulphuric acid in order to extract the thorium and other rare earths, the barium sulphate and mesothorium sulphate are left behind in the residue and can be recovered from the coarse silica, etc., by sliming. The crude concentrates so obtained can be still further purified by fusion with a mixture of caustic soda and sodium carbonate, by which means the silica is converted into sodium silicate and can be washed away from the barium-mesothorium carbonates, or the silica can be eliminated by the use of hydrofluoric acid. The refined sulphate so obtained is purified by the same methods described under the refining and purification of radium.

Actinium.—Actinium was discovered by Debierne in the iron group separated from pitchblende, shortly after the discovery of radium and polonium. Actinium itself is probably rayless, but its first product, radioactinium, has a half-life period of 18.8 days. Actinium preparations when first made increase enormously in activity over a period of several months. It is, therefore, comparatively easy to overlook its presence, unless the preparations are kept and their activity tested periodically. Actinium is easily obtained with iron and rare earths by precipitating barium as sulphate in an acid solution; and this accounts for its presence in pitchblende residues. In working these up, the acid solutions, after removal of polonium by means of hydrogen sulphide, are oxidized and precipitated with ammonia, the actinium being precipitated and the radium and barium, of course, remaining in solution. The precipitate may be extracted with dilute hydrofluoric acid, the insoluble part consisting of La, Di, Ce, and Th retaining most of the actinium. The rare-earth element most closely associated with actinium is lanthanum. In the presence of ammonium

[1] This is true only when the uranium and the radium are in equilibrium. In other cases it represents the theoretical amount of uranium in equilibrium with the radium actually present. In pitchblende, since it is a primary mineral, the ratio of uranium to radium is constant, 1 g. uranium = 3.3×10^{-7} g. of radium, or 2000 lb. U_3O_8 = 331 mg. $RaCl_2$, and if the percentage of uranium is known by analysis the amount of radium present can be calculated directly. In carnotite and other recent uranium minerals, the equilibrium ratio is not constant and the radium present has to be found by experiment.

salts the precipitation of actinium is far from complete, but it is completely precipitated in the presence of manganese from basic solutions.

Polonium. (Radium F.)—Polonium is one of the short-lived radioelements having a half-life of 140 days and giving off alpha rays only. Its discovery was due to the fact that it is closely allied to bismuth and precipitates with bismuth in the second group. For this reason it is easily separated from radioactive minerals in crude form by digesting radium containing residues of pitchblende or carnotite ore itself with hydrochloric acid. A part of the polonium is dissolved and may be precipitated with hydrogen sulphide. The polonium may be purified (1) by fractional precipitation from solutions made very acid with hydrochloric acid, the polonium being enriched in the precipitate; (2) by fractional precipitation of the basic nitrate with water, the precipitate being enriched; (3) by sublimation *in vacuo*, the polonium being more volatile. By immersing a plate of bismuth, silver, copper, etc., in a hydrochloric acid solution, the polonium is practically completely precipitated. The theoretical quantity of polonium in minerals is 1 g. for 14 tons of uranium element, assuming that no radium emanation escapes from the mineral. As such a condition never exists in nature, the actual amount is less than the theoretical.

Radiolead. (Radium D.)—There are three kinds of lead: (1) one representing the final disintegration product of the uranium series; (2) the final disintegration product of the thorium series; and (3) ordinary lead, which so far as is known, does not owe its origin to radioactive changes. The first has an atomic weight of 206, the second 208, and ordinary lead 207. Since radiolead, or radium D, resembles lead perfectly in all its chemical reactions, in the treatment of uranium minerals it cannot be separated from the lead which is found in such minerals. It is, therefore, obtained in association with this lead when the latter is precipitated during the refining of the radium-barium sulphate. Common commercial lead contains traces of radium D and is more distinctly radioactive than most other metals. For this reason, in making instruments, a very old lead should, if possible, be employed, as in this the radioactive constituents will largely have decayed. Another source of radium D is old radium, in which the radiolead has to a certain extent accumulated. If, however, a sample of this element is required in concentrated form, the best method is to remove the emanation periodically from a radium solution kept in an airtight vessel and introduce the emanation into a closed vessel. As the emanation decays, the radiolead will be formed and will be deposited on the sides of the vessel. This can then be dissolved by acid and precipitated by ammonia or other lead precipitants, provided a small amount of lead salt is introduced in order to give a precipitate sufficiently large to be handled.

CHAPTER XXIV

TIN

By R. L. Hallett[1]

Physical Properties.[2]—Tin is a relatively soft silver-white metal with a brilliant luster. Its atomic weight is 118.7. It is not very ductile—it is too soft to permit drawing. It is very malleable and may be rolled into thin sheets, the property which is utilized in the manufacture of tinfoil. The tensile strength of tin is low, being somewhat higher than that of lead but lower than most of the other metals. Most impurities tend to increase the tensile strength of tin, but they also decrease its malleability and ductility.

The specific gravity of tin varies with the method of preparation; the specific gravity of cast tin is about 7.29, of rolled or extruded tin about 7.31. The melting point of tin is 232°C., and the boiling point has been reported to be about 2260°C.

Most of the impurities usually found in tin tend to make it harder and more brittle. Many of them tend to raise its melting point, but some of them (such as lead) form eutectic mixtures with tin and lower its melting point.

When tin is exposed to low temperatures, the physical character of the metal seems to undergo a complete change, probably a molecular change, during which the solid metallic form is changed to a gray powder made up of small grains. This form is known as the "gray modification" and seems to be an allotropic modification of tin. The change may take place at temperatures below 18°C. The specific gravity of the gray modification has been reported to be about 5.8.

Tin in its ordinary form is somewhat crystalline in structure, the cast form being more crystalline than the rolled form. When a bar of tin is bent it gives a characteristic "cry," a slight cracking noise, probably caused by the friction of the crystals on each other.

Chemical Properties.—At ordinary temperatures, metallic tin is not readily acted on by many chemical substances. The action of the elements of the atmosphere is slight, accounting for the wide use of tin as a protective coating for iron and steel in the well-known form of tin plate.

Cold dilute hydrochloric acid dissolves tin slowly, and the action is more rapid when hot concentrated acid is used. Stannous chloride is produced and hydrogen is given off in the reaction.

Dilute sulphuric acid slowly dissolves tin with the evolution of hydrogen, and hot concentrated sulphuric acid dissolves tin rapidly with the evolution of sulphurous anhydride and the separation of sulphur.

Very dilute nitric acid dissolves tin without the evolution of gas, forming stannous nitrate and ammonium nitrate, and strong nitric acid rapidly converts it into metastannic acid, which is insoluble in most other acids. Aqua regia (nitrohydrochloric acid) dissolves tin readily, forming stannic chloride.

Tin usually acts as a base but sometimes as an acid. Tin oxide, SnO_2, is not appreciably attacked by most acids, but at high temperatures tin oxide reacts readily

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[2] References are to similarly numbered references in the Bibliography at the close of the chapter

with silica to form the silicates. When tin oxide is heated with some strongly basic substances, such as fixed alkalies, stannates of the bases are formed.

Alloys.—Tin readily forms alloys with most of the other metals. Some of the alloys are of great commercial and industrial value, but the use of tin in alloys is second in importance to its use in tin plate.

Perhaps the most important alloys of tin are those with antimony and copper in bearing metals, with lead in solder, with lead and antimony in type metal, with lead in terneplate, with copper and sometimes zinc in bronze and many other alloys used for minor purposes.

The only tin alloys that greatly affect the metallurgy of tin are the alloys of iron. Tin alloys readily with iron, which fact is said to account largely for the success in plating iron with tin.

The tin-iron alloys formed in some tin metallurgical operations are known as "hard-head." They have very high melting points and introduce certain difficulties in the metallurgy of tin. The best known hard-head alloy is $FeSn_2$. The alloy containing 50 per cent tin and 50 per cent iron has the lowest melting point, which is given as 1140°C.[2].

Tin Ores.—By far the most important ore of tin is the mineral cassiterite, which is tin dioxide, SnO_2. It contains 78.6 per cent tin and 21.4 per cent oxygen. It crystallizes in the tetragonal system and has a hardness of 6 to 7. The specific gravity is 6.8 to 7.1. The color is brown or black, sometimes red, gray, white, or yellow.

The occurrence of tin as the mineral stannite, a triple sulphide of tin, copper, and iron, has been reported and is of interest, but no deposits of commercial value have been found. A number of other tin minerals have been identified in various places, but are of scientific interest only.

Tin oxide (cassiterite) is the commercial ore from which the tin of commerce is produced. It occurs in many parts of the world in original deposits in the form of veins or lodes, and also in transported alluvial or placer deposits. The occurrence in these two forms gives rise to the two names for the ore: "vein tin" and "stream tin," designating the vein and the placer deposits.

Tin ores also are referred to as "tin stone," "washed tin," "tin sand," "black tin," and "barilla," the different terms being used in different localities where the nomenclature probably has been developed locally.

Minerals containing other metals often are found associated with cassiterite in the original vein deposits, but in the placer deposits the tin ores usually are fairly pure because, while cassiterite is practically unaffected by the action of the elements of nature that decompose the original vein formations and transport the decomposed material to the placer deposits, many of the other minerals are altered to such an extent that the metals contained in them are readily washed away and are not found associated with the cassiterite in the placer beds.

The metals often found associated with cassiterite in vein deposits are Pb, Bi, W, Sb, Zn, Cu, Ag, As, and Fe. While the tin almost invariably occurs as the oxide, the other metals when present are nearly always in the form of sulphides, except arsenic and tungsten, which usually occur in the form of arsenides and tungstates.

Occurrence.—Tin has been found in many parts of the world, but in some large areas (such as practically the whole of North America) no tin deposits of any great commercial value have been discovered up to the present time.

The large and valuable tin deposits of the world are found in the Malay States (comprising the Malay Peninsula), Netherlands East Indies, Bolivia, Thailand, Belgian Congo, China, Nigeria, and Burma with minor deposits in Australia, Argentina, Cornwall, Indo-China, Japan, Portugal, and elsewhere. The tin ore produced in the Malay States, Netherlands East Indies, Thailand, Belgian Congo, Nigeria, and

Burma is very largely from placer deposits. The important ore deposits in Bolivia, China, and Cornwall are mostly vein formations.

Up to and including the eighteenth century, civilization secured its tin supply mainly from Cornwall in England and from Saxony and Bohemia in Europe. Early in the nineteenth century the European deposits became practically exhausted, but the Cornwall deposits increased in production and importance, and together with the placer deposits of the Netherlands East Indies, formed the main supply until production from the Malay States began to come in toward the end of the nineteenth century and the early part of the twentieth century. At the present time, the Cornwall deposits have become greatly depleted. During the first twenty years of the twentieth century, the Malay States became the largest producer of tin and have occupied that position continuously until the present time. The production of tin from Bolivia began to be a material factor toward the end of the nineteenth century, and at the present time the production from both the Netherlands East Indies and Bolivia is second only to that of the Malay States.

The production from the different localities during the years 1936 to 1940 as given in "Minerals Yearbook" is given in Table 1.

TABLE 1.—WORLD'S PRODUCTION OF TIN
(Tin content of ore in long tons)

Country	1936	1937	1938	1939	1940
Belgian Congo	6,301	8,084	8,820	9,663	7,600
Bolivia	24,052	25,128	25,484	27,211	37,923
Malay States:					
Federated	64,680	75,117	41,206	49,525	85,384
Unfederated	1,979	2,075	2,041	1,994	
Straits Settlements	58	72	114	206	
Netherlands East Indies	30,728	39,133	27,299	27,755	44,447
Nigeria	9,648	10,782	8,977	9,427	12,012
Thailand	12,633	15,786	14,704	17,325	17,447
Burma	4,546	4,636	4,412	4,500	5,500
Australia	3,027	3,256	3,329	3,500	
China	11,082	12,871	11,605	10,422	6,349
Other countries	10,266	11,160	11,909	11,172	15,038
Total	179,000	208,100	159,900	172,700	231,700

During the years preceding the First World War much of the tin ore from the Malay States was smelted in Singapore and Penang (Straits Settlements), and much of the tin ore mined in the Netherlands East Indies (the Islands of Banka and Singkep) was smelted in Holland. Practically no tin ore of the Far East has been smelted in the United States because of the foreign government restrictions which have prevented the development of an American tin-smelting industry with the ores from that source.

Before the First World War a large proportion of the Bolivian tin ore was smelted in England and the remainder in Germany. As the war progressed, Germany was eliminated because of her inability to secure Bolivian ore, and for several years during the war the tin ore from Bolivia was smelted almost entirely in England and in the United States, each country receiving about half the Bolivian output.

The tin-smelting industry in the United States was not started until 1916, but rapidly developed thereafter until in 1923 it had reached an annual tin-smelting

capacity of about 20,000 tons of fine tin. During 1923 the tin-smelting companies in the United States were forced to abandon their operations, owing to their inability to meet the cheaper costs of smelting tin ore in Europe, chiefly in England and Germany.

From 1923 to the time of the Second World War a large part of the Bolivian ore production was smelted in England, although some was smelted in Germany and Belgium. After the start of the Second World War the Longhorn tin smelter was constructed in Texas by the American government. When it was completed about half the Bolivian ore was smelted in England and half at the Texas smelter.

Prior to 1916 the only tin produced by smelters in the United States was the secondary metal obtained from the smelting of dross, scrap, and refuse. Smelting of dross and the recovery of secondary metal still is and will continue to be an important industry in the United States, and the amount of tin so produced is probably about 30 per cent of the primary tin used in the United States.

FIG. 1.—Open-cut tin mines, Straits Settlements.[1]

Consumption.—The world's recent peacetime annual production of primary tin has been about 180,000 long tons, of which about 40 per cent has been consumed in the United States. Of the tin consumed in the United States about 50 per cent is used for tin and terneplate, about 25 per cent for bearing metals and solder, and the remainder in various industries where tin in different forms is required. The United States, therefore, occupies the unique position of being the country which is the largest consumer of tin, but which, aside from the insignificant quantity coming from Alaska, produces practically no tin from natural deposits and must depend entirely on supplies from foreign countries.

Grades of Tin.—With tin, perhaps more than with any other metal, the location and the character of the ore deposits from which the tin is obtained determine to a large extent the quality and the use of the tin that is produced. In metallurgical recovery operations most metals are so completely refined that they are recovered eventually in pure form generally suitable for the purposes for which such metals are used. The methods of refining are usually such that the ores from all sources are amenable to the methods and pure metals are produced, no matter what impurities may be associated with the metals in the original ore deposits.

[1] Figures 1 to 5 inclusive are used by courtesy of Malay States Information Agency.

With tin the conditions are quite different. The selection of tin for various uses depends greatly on the impurities that the refined tin contains and, because of the difficulty of removing the metallic impurities in the tin-refining process, the success in refining depends to a considerable extent on the purity of the original tin deposits and the kind and amount of other metals associated with the tin in the original ore.

For this reason, tin from the ores obtained from certain localities has established a reputation for quality not because the metallurgical methods of recovery and refining of the tin are superior, but because the tin ores produced in those localities contain such small amounts of associated metal impurities that fairly simple metallurgical methods produce refined tin of great purity.

Tin from other sources where the ores are contaminated by large amounts of other metals is refined with great difficulty and even after refining to the greatest possible degree permitted by competitive cost is usually not so pure as the tin from the localities where the ore does not contain the impurities in the original ore deposits.

FIG. 2.—Open-cut mine, Straits Settlements.

This condition has developed the present tin situation, where reputation of brand, resulting partly from metallurgical treatment but largely from purity of the original ore deposits, is the first consideration in purchasing the metal.

The metallurgical methods used in different smelting plants have been specially developed to treat the different kinds of ore obtained from different localities and for that reason great differences in metallurgical processes and methods of treatment have resulted. These methods have been carried on for such a long time that they have become more or less standardized in the various smelters, and the different brands of tin are fairly uniform in regard to the kind and amount of impurities they contain. Tin made from ore from different parts of the world varies somewhat in purity, and the uses of tin also vary, as some uses seem to require tin of great purity, while others are satisfactorily met with tin that is somewhat less pure.

The kind as well as the amount of impurities contained in tin is an important consideration. While there are undoubtedly characteristic differences in the composition of tin produced from the different ores, taken altogether, the differences are not great when refining has been properly done. For many years tin has been marketed under the brand or trade name of the producers. This has led to the distinct classification according to brand, and each brand has assumed its own relative

TABLE 2.—TYPICAL ANALYSES OF THE PRINCIPAL BRANDS OF PRIMARY TIN[1]

Brand of tin	Smelting country	Tin	Lead	Antimony	Copper	Arsenic	Iron	Bismuth	Nickel and/or cobalt	Sulphur	Silver	Cadmium
Pass, No. 1	England	99.98935	0.0008	0.0055	0.0005	0.001	0.0025	0.0001	.....	0.00025		
Chempur	England	99.98611	0.0082	0.0032	0.0007	0.0001	0.0005	0.0009	.....	0.00029		
Banka	N.E.I.	99.983	0.0001	0.0101	.....	Trace	0.0064					
Un. Min. du H. Katanga	Belgium or Congo	99.966	0.012	.....	0.013	0.006	0.003	Trace				
O. T. Lempriere & Co.	Australia	99.942	0.010	0.020	0.018	0.006	Trace	0.002	0.002	Trace	......	(Zinc, trace)
Pyrmont	Australia	99.938	Trace	0.017	0.022	0.019	Trace	......	.....	0.004		
Billiton	N.E.I.	99.934	0.019	0.018	0.003	0.018	0.007	0.001				
Penpoll special refined	England	99.925	0.038	0.005	0.0102	0.009	0.004	0.004	0.004	....	0.001	
Mellanear 99.9%	England	99.915	0.037	0.013	0.009	0.008	0.004	0.007	0.007			
Eastern Smelting Co.	Straits Settlements	99.907	0.024	0.003	0.003	0.035	0.008	0.009	0.003	0.008		
Straits Trading Co.	Straits Settlements	99.895	0.029	0.004	0.025	0.031	0.009	0.007	Trace			
Murex Refined	England	99.895	0.036	0.020	0.012	0.023	0.008	0.006	.....	Trace	......	(Zinc, trace)
Hawthorne Refined	England	99.891	0.028	0.010	0.028	0.029	0.010	0.004	Trace			
Tulip Refined	Holland	99.870	0.038	0.041	0.008	0.031	0.009	0.003				
Yunnan Tin Corp. Ref.	China	99.870	0.044	Trace	0.010	0.056	0.014	0.0056	. . ..	......	0.0004	
Mellanear Refined	England	99.827	0.065	0.028	0.022	0.025	0.005	0.013	0.013	....	0.002	
Cornish Refined	England	99.820	0.065	0.022	0.034	0.030	0.005	0.010	0.014			
Dutch L & F 99.5%	Holland	99.530	0.152	0.185	0.038	0.079	0.009	0.007				
Wing Hong No. 1	China	99.343	0.434	0.031	0.052	0.040	0.010	0.007	0.072	0.011	Trace	
Mellanear L & F Comn.	England	99.206	0.468	0.136	0.081	0.065	0.006	0.012	0.014	....	0.008	0.004
Cornish L & F Comn.	England	99.180	0.440	0.139	0.118	0.080	0.008	0.020	0.015			
Penpoll L & F Comn.	England	99.158	0.386	0.190	0.129	0.078	0.006	0.019	0.017	....	0.012	0.005
Dutch L & F 99%	Holland	99.100	0.412	0.289	0.082	0.089	0.014	0.014				
Dutch L & F 98%	Holland	98.100	1.37-	0.273	0.122	0.085	0.028	0.017				
Longhorn 3-Star	United States	99.80 or over	0.020	0.037	0.025	0.020	0.004	0.004	0.005	0.005	0.0005	Trace
Longhorn 2-Star	United States	99.50 to 99.[illegible]										
Longhorn 1-Star	United States	99.00 to 99.49										

[1] Figures for brands other than Longhorn taken from publications of the International Tin Research and Development Council. Figures for Longhorn 3-Star taken from "Metal Statistics." Figures for Longhorn 2-Star and 1-Star taken from United States Government information releases.

importance in accordance with its reputation for uniformity and the kind and amount of impurities it contains.

The principal brands of pig tin produced by the tin smelters of the world together with the countries in which the smelters are located and typical average analyses of each brand are given in Table 2.

Prices.—Under normal conditions, where the prices are controlled by supply and demand, the principal markets are in London and New York, and prices are established at those points. Prices in London and New York are usually fairly near together, the London price being just enough under the New York price to represent

FIG. 3.—Hydraulic mining, Straits Settlements.

approximately the cost of freight from London to New York. The average yearly prices of Straits tin for prompt delivery in New York as published in *Minerals Year book* are given in the following table:

PIG TIN PRICES IN NEW YORK

Year	Average, Cents per Pound
1936	46 42
1937	54 24
1938	42 26
1939	50.18
1940	49 82

Mining.—The mining methods used to remove the tin ore from the natural deposits depend to a large extent on the character of the deposits, whether vein or placer, and to a less extent, on the location, kind of labor available, climate and other local conditions.

The vein deposits are worked by mining methods very similar to those used for the hard-rock mining of the ores of other metals.

The placer deposits are mined with open cuts and by hydraulic sluicing and dredging. Some of the open-cut mining in the Far East is done in a crude and elementary manner, but much of the hydraulic sluicing and dredging is carried on according to the best modern mining methods.

The sand and gravel from the open-cut mines usually are treated in sluice boxes and sometimes even in hand pans to concentrate the cassiterite and wash out the worthless material. Typical open-cut mines in the Malay States are shown in Figs. 1 and 2.

Where hydraulic sluicing methods are used, the placer ground often is broken up with modern "giants" or "monitors," and the sand and the gravel are washed through sluice boxes to concentrate the tin mineral. Hydraulic mining in the Malay States is shown in Figs. 3 and 4.

Dredging is done with floating boat dredges following practice similar to the dredging of placer ground in other parts of the world.

The tin ore from vein-mining operations is milled at the mines. It is first crushed to break the cassiterite away from the associated minerals, and it sometimes is necessary to crush some of the gravel from placer ground to accomplish the same end.

The mined and crushed ore is then treated in sluice boxes, hand pans, or, in the more modern operations, with standard wet-concentrating machinery. As the specific

Fig. 4.—Hydraulic mining, Straits Settlements.

gravity of most of the gangue minerals is lower than the specific gravity of cassiterite, the mechanical concentrating treatment removes most of the gangue and earth and leaves the tin in the form of cassiterite concentrates, usually containing more than 60 per cent of tin. Hand picking sometimes precedes the wet-concentration treatment. In the purchase of tin concentrates by the English tin smelters, the treatment charge is usually based on concentrates containing 60 per cent tin with an increased treatment charge if the concentrates contain less than 60 per cent tin, and a decreased charge if they contain more than 60 per cent tin.

If the ore is obtained from placer ground, the tin concentrates resulting from the mechanical treatment are usually fairly pure, but if the ore is obtained from vein deposits, the concentrates may be contaminated with small amounts of the sulphides of other metals.

Preparing the Ore for Smelting.—Modern smelting reduction methods as applied to the metallurgy of tin are fairly efficient and economical, but because of the metallurgical and chemical characteristics of tin, the refining methods in general use are not entirely satisfactory and fail to remove completely the metallic impurities which are reduced with the tin in the smelting process. For this reason it is often necessary to treat specially the tin concentrates from some localities so as to remove the metal

impurities they contain and make them suitable for smelting. Tin concentrates from other localities, where the original ore deposits do not contain the metal impurities, require much less treatment to prepare them for smelting, and some tin ores are smelted successfully after simple mechanical concentration to remove the gangue.

Generally speaking, the tin concentrates from vein deposits, particularly those of Bolivia, require the most extensive preparation before smelting, and the tin concentrates from placer deposits require the least preparation.

A number of methods are used to remove the metal impurities from the tin concentrates before smelting, and these methods might be classified somewhat broadly as follows: (1) roasting, followed by further mechanical separation of minerals that are broken away from the cassiterite by roasting, or are altered in such a way as to change their specific gravity and make them more amenable to mechanical concentrating methods; (2) roasting, followed by leaching with water or with acid solution; dilute solutions of sulphuric acid and hydrochloric acid are sometimes used in this process; (3) heating with sodium carbonate or salt cake (sodium sulphate) followed by leaching with water; (4) chloridizing roast with sodium chloride (salt) followed by leaching with water or hydrochloric acid; (5) the removal of metal impurities present in the form of sulphides, by oil flotation.

Roasting Followed by Mechanical Concentration.—Cassiterite is not decomposed or appreciably altered when calcined at a red heat, but many of the associated minerals containing other metals are so altered as to make further mechanical separation possible. During the roasting process, much of the sulphur and arsenic and some of the antimony are volatilized and removed. After roasting is completed, the resulting material contains tin oxide, substantially in its original form; oxides of iron, zinc, bismuth, and copper; sulphate of lead; some arsenate of iron; and small quantities of more or less unaltered sulphides of the metals, together with some unaltered tungsten compounds and minor amounts of other mineral products. The volatile products, particularly arsenious oxide, sometimes are collected and recovered in baghouses or other dust-collecting equipment.

Some of the associated minerals are broken away from the cassiterite and freed from it by the roasting treatment. When the calcined material is further treated by mechanical concentration methods, some of the altered or separated minerals are removed, producing purer and cleaner cassiterite concentrates.

The roasting of tin concentrates is done in roasting furnaces of many types, more or less following roasting practice used in the metallurgy of the ores of other metals. The roasting may be done in hand-rabbled reverberatory furnaces or in mechanical furnaces, of which many types are in use. Perhaps the most popular furnaces for the roasting of tin ore are those of the rotating-cylinder type, such as the Oxland and Hocking and the White-Howell furnaces These furnaces are made with a heavy steel or cast-iron cylindrical shell 30 to 40 ft. long and 4 to 6 ft. in diameter, lined with firebrick. They are placed in a nearly horizontal position and are equipped with bearing rings that run on friction rollers. The furnaces are driven by gears attached to the shell and rotate at fairly low speed.

The charge end is slightly higher than the discharge end, which arrangement causes the material in the furnace to pass slowly through as the furnace rotates. Coal or oil is used for fuel, and the heat is usually admitted at the discharge end.

Roasting furnaces of the fixed-hearth revolving-rabble type also are used. Furnaces of this type are the Wedge, Herreshoff, MacDougall, Ridge, Pearce Turret, Merton, and others of similar construction. Most of these furnaces have fixed circular hearths with revolving rabble arms mounted on a central vertical rotating shaft. The arms are fitted with rabbles which slowly stir the charge and carry it around the hearth as the rabble arms revolve. Some of the furnaces of this type have but a

single hearth, while others have several hearths, one above another, all operated by the same central shaft. The top of the furnace sometimes is used as a drying hearth to remove the moisture before the charge is fed to the first enclosed hearth. The furnaces usually are built of firebrick, with arched-roofed and sometimes arched-floor construction.

The roasting problems involved do not differ materially from those encountered in the roasting of the ores or other metals. The larger multiple-hearth roasting furnaces and the larger rotating-cylinder furnaces have about the same capacity, and about 1 ton of tin concentrates per hour can be roasted satisfactorily in such furnaces. The fuel consumed is 100 to 300 lb. of coal per ton of tin concentrates roasted. It generally is desirable to crush the ore or concentrates before roasting, and satisfactory results usually are obtained if the material is crushed to pass about a ¼-in. screen. To maintain proper roasting conditions, it usually is desirable to keep the roasting furnaces at temperatures of 550 to 650°C. The type of furnace, kind of fuel, and roasting cost depend on the location, character of labor, kind and amount of impurities in the tin concentrates and other conditions that affect roasting problems in general and that have been described fairly completely in the first volume of this work.

Roasting Followed by Leaching.—Instead of mechanical concentration following the roasting of tin concentrates, the calcined material sometimes is leached with water or acid solution to remove products that have been made soluble by the roasting treatment.

Leaching with water sometimes emoves certain soluble compounds, but leaching with dilute acid solutions is more effective, as some of the products formed during the roasting process are readily soluble in acids, although insoluble in water.

Heating with Sodium Compounds.—Some tin concentrates contain tungsten compounds, which are not greatly affected by simple roasting. When these compounds are heated with sodium carbonate or sodium sulphate to about 600°C., sodium tungstate is formed. If the process is carried beyond the stage of the formation of sodium tungstate, some sodium stannate is produced, and for that reason an excess of sodium carbonate or sodium sulphate should be avoided.

In this process the tungsten minerals react with the sodium compounds to form sodium tungstate, which is soluble in water and may be removed by leaching the treated material with water in a properly constructed vat. The sodium tungstate may be recovered from the solution by evaporation. After being suitably purified, it has a ready market.

The process should be controlled by regulating the amount of sodium carbonate or sodium sulphate so that it will be present in sufficient quantity to combine with the tungsten but will not be present in excess so as to combine with some of the tin.

This process has been used in several localities, but the results have not been entirely satisfactory, and the process is not used to any great extent at the present time. The removal of tungsten minerals by hand picking is perhaps the most satisfactory method and is the one generally used when it is found necessary to remove the tungsten minerals before smelting.

Jennings and Dolan[3] have proposed a method for removing impurities from tin concentrates by heating the concentrates with acid sodium sulphate (bisulphate) instead of salt cake. They state that the cassiterite is not affected by this treatment and that many of the other impurities are converted to soluble sulphates and may be leached out with water.

Chloridizing Roast.—When the tin concentrates are contaminated with sulphides of the other metals, a chloridizing roast, followed by leaching, sometimes is used to purify the concentrates before they are smelted. When the sulphides of many of the common metals are roasted with salt in an oxidizing atmosphere, the sulphur becomes

oxidized and combines with the sodium of the salt as sodium sulphate, while the metals combine with the chlorine in the form of chlorides. Cassiterite is practically unaffected by the chloridizing roast.

In the chloridizing metallurgical operations carried on in connection with the treatment of ores, it has been found that the chlorides of some of the metals are fairly volatile, and in the chloridizing roast such metals as bismuth, lead, arsenic, antimony, and silver may partly be removed in the form of fume. The chlorides of some of the metals that remain with the calcined concentrates are soluble in water or dilute acid and may be removed by suitable leaching and washing.

Leaching of the calcined concentrates with water or dilute acid usually is done in wooden or rubber-lined vats, properly constructed and in some cases fitted with filter bottoms.

The chloridizing roast is carried on in furnaces similar to those used for dead roasting, the principal difference being that 1 to 5 per cent of salt (NaCl) is mixed with the ore or concentrates before they are charged to the chloridizing furnace. (See the chapter on Chlorine in Metallurgy for further information on this subject.)

Oil Flotation.—The separation of metal sulphides from other minerals by means of oil flotation has been perfected and has become a most important and extensively used metallurgical operation for the treatment of ores. Flotation is used to great advantage in the purification and preparation of some tin ore or concentrates for smelting. The sulphides of most of the common metals are floated without difficulty, and cassiterite is practically unaffected, permitting separation of the metal sulphides from the tin mineral.

In this well-known process the finely ground ore is mixed with water and is agitated violently. Oil in small amount, sometimes only a fraction of 1 per cent, is added, and the agitation is continued until a heavy froth forms and floats on the surface. Minute oil bubbles become attached to the small particles of metal sulphides because of the surface-wetting property of the oil for sulphide minerals, and in this way the oil brings the particles of sulphide minerals to the surface and causes them to float in the froth. This action produces a separation of the metal sulphides from the cassiterite and gangue, which sink in the water in which the flotation is carried on.

Different kinds of oil are used for different sulphide minerals, and by judicious selection of the oil and certain chemical additions to the flotation water, not only complete flotation of practically all the sulphide minerals is obtained, but it is also possible to produce selective flotation which removes one or more sulphide minerals and leaves the other sulphides unfloated. A further change in conditions renders additional sulphide minerals subject to the flotation action, and they may then be removed as separate concentrates.

Summary of Ore-preparation Methods.—The common metals which, in the form of sulphides, are often associated with cassiterite and remain as impurities in cassiterite concentrates are Pb, Bi, Sb, Zn, Cu, and Fe. Arsenic is often present in the form of arsenides or arsenates of iron or other metals. Tungsten, when present, is usually in the form of tungstate of lime or other bases.

Mechanical concentration removes the gangue, but usually does not successfully remove the metal sulphides, because the specific gravities of most of the metal-sulphide minerals are not sufficiently different from the specific gravity of cassiterite to make mechanical separation possible.

Roasting will remove most of the sulphur and arsenic in the form of sulphurous and arsenious anhydrides, converting the metals with which they were previously combined into oxides. The sulphides of iron, copper, bismuth, and zinc are converted to oxides by roasting, and sulphide of lead is largely converted to sulphate. After roasting, the oxides of bismuth, zinc, and copper may be removed by leaching

with dilute acid. Tungsten may be removed by heating with sodium carbonate or sodium sulphate followed by leaching with water. Lead, bismuth, antimony, and silver may be removed by a chloridizing roast, followed by leaching with acid. Practically all the metal-sulphide minerals may be removed by oil flotation. It will, therefore, be seen that a suitable selection of one or more of the purification methods which have been described will enable the metallurgist to remove most of the metal impurities contained in the tin concentrates and thus obviate their reduction with the tin in the smelting operation.

Tin is a high-priced metal, and in comparison with some of the other common metals, the production of tin is small. No very large tonnage of tin ore or concentrates is smelted at any one tin-smelting plant.

The tin ores or concentrates are usually shipped from the mines in sacks and are sampled before going to the storage bins or to the treatment or smelting departments. It is the usual practice to sample each lot by taking each tenth sack and reducing the sample so obtained by coning and quartering or with a mechanical sampler until a sample of suitable size for assay is obtained.

Because the tin is so valuable, the concentrates must be handled carefully to prevent loss of dust in sampling, during the transfer to the storage bins, and while charging to the roasting and smelting furnaces.

Smelting.—The tin metallurgist is fortunate in receiving the tin in the form of oxide instead of in the form of more complex compounds which might introduce metallurgical difficulties. The reduction of tin from its oxide to its metallic form is not difficult, as the reduction takes place readily when tin oxide is heated to fairly high temperatures in the presence of reducing agents, such as carbon. An excessively high temperature is not required to bring about the reduction of the tin to the metallic form. The temperature required for smelting is largely determined by the composition of the slags which are formed; for the smelting temperature must be such as to produce liquid slags that will permit the reduced tin to settle and collect in the bottom of the furnace.

The smelting of tin offers problems similar to those encountered in the smelting of ores of other metals, and the general statement might be applied to all reduction smelting of this type that the results are always better if the smelting temperature is reached as quickly as possible.

Two distinctly different smelting methods are followed, and the two methods make use of furnaces of entirely different types. In one method the tin concentrates are smelted in shaft or blast furnaces, and in the other they are smelted in reverberatory furnaces. The older method and the one that was in most general use during the early life of the tin-smelting industry of the world is shaft- or blast-furnace smelting.

Reverberatory smelting of tin ores and concentrates did not come into use until well along in the eighteenth century and did not reach full development until the middle of the nineteenth century, but it is now the most generally used process, particularly in the larger smelting plants.

In the smelting of tin ores and concentrates, the end desired is to produce as much reduced metal as possible and to make slags of such composition that they will be liquid at the smelting temperature and permit the reduced tin to settle through them. It also is desired to produce slags as low in tin as possible, as the principal loss in tin smelting is in the tin carried away by the slags.

Tin smelting does not differ materially from the smelting of ores of other metals, except that the reduction is simpler, and, because of the absence of appreciable quantities of sulphur, matte usually is not formed. The smelting of tin would appear to be a fairly simple process and, as far as the actual smelting operation is concerned, the process is not complicated. The great difficulty in the smelting is introduced

by the fact that tin oxide combines readily with silica to form silicates of tin, and during the smelting of tin concentrates mixed with flux and fuel, a considerable amount of tin invariably combines with silica and goes into the slag in the form of readily fusible silicates of tin mixed with the other more or less complex silicates that make up the slag. On the other hand, if an extremely basic slag should be used, tin will act as an acid, and again enter the slag.

In smelting ores of lead and copper, it is comparatively easy with the production of metal, matte, and slag in the case of lead smelting, or with matte and slag in the case of copper smelting, to hold practically all the lead and copper in the metal or matte, as the case may be, and prevent it from going into the slag. In tin smelting, however, while a large proportion of the tin is reduced and recovered in the form of metal, an unduly large amount invariably fluxes with silica and goes into the slag. The amount of tin contained in practically all slags from the primary smelting of tin concentrates is so extremely high that such slags cannot be discarded but must be re-treated for their tin contents. As it is necessary to resmelt the first-run slags, it is important to use only a small amount of fluxing material in the smelting of tin concentrates so as to produce a minimum amount of slag.

The smelting of tin, therefore, embraces three distinct stages: the primary smelting of the tin concentrates in a blast furnace or in a reverberatory furnace with the proper addition of fluxes and fuel; the re-treatment of the first-run slags to recover the tin they contain; and, finally, the refining of the reduced metallic tin to remove the metal impurities that are reduced with the tin in the smelting process.

Smelting in the Blast Furnace.—Historical records seem to show that tin was first recovered by smelting cassiterite in small, crude, hand-operated shaft furnaces that required some draft. Natural draft probably was used in some of the early furnaces; later on forced draft, created by hand-operated blowers, was introduced.

Some very crude small furnaces are still in use in the Far East, where fairly pure cassiterite mixed with charcoal is fed into small shaft furnaces. No scientific attempt is made to produce slags of any particular composition, and the amount of impurities in the ore which is being treated is so small that fairly high reduction of metallic tin is obtained.

Some of the original shaft furnaces used in the Far East were simply hollow pits dug in the ground. The blast for such furnaces often was obtained by means of hand bellows. Some of the smaller Chinese shaft furnaces consist of bamboo forms lined with clay. A small Chinese tin-smelting furnace operated with a hand blower, such as is still being used in many semicivilized portions of the Far East, is shown in Fig. 5.

With the introduction of the tin ores from Cornwall, the metallurgy of tin in England received much scientific thought, and a large amount of metallurgical skill was devoted to it. The crude furnaces used in the Far East soon were replaced by larger furnaces, and the old familiar blast furnace (known as the "Cornish tin castle") was developed. This was a shaft furnace constructed entirely of stone or brick and, in its best form, was operated with positive blowers of the Roots type. Charcoal was largely used for the fuel during the early development of tin smelting in England, but was later replaced by coke. The shafts of these furnaces were fairly low, and the furnaces had comparatively small capacity.

At the present time some modern steel water-jacketed blast furnaces are in use in different parts of the world where tin concentrates are smelted in shaft furnaces. The blast furnaces have a fairly low shaft and are operated with comparatively low blast pressure. With the exception of the low shaft, the furnaces are of the modern lead-smelting type, and metal and slag are produced according to regular blast-furnace smelting practice.

Blast furnaces for the smelting of tin concentrates are operated with coke fuel and are fluxed with limestone, silica, and other materials to produce easily fusible slags similar to the slags made in the smelting of the ores of other metals.

The charging, fluxing, and operation of tin blast furnaces correspond approximately to similar operations in the blast-furnace smelting of other metals. The principal difference between tin smelting and the smelting of other metals is in the tin which the first-run slags contain.

While the formation of tin silicates as part of the slags is an economic difficulty, it does not introduce any metallurgical troubles, as the silicates of tin have low melting points and do not hinder the satisfactory operation of the furnaces. Slags made in blast furnaces smelting tin concentrates are usually high in tin and may often contain 10 to 25 per cent tin in ordinary practice.

A brick-lined settler or forehearth sometimes is used to collect the slag and metallic tin as they are tapped from the blast furnace. The slag usually overflows from the

FIG. 5.—Small Chinese blast furnace.

settler into slag pots, which are taken away, and the molten slag is poured into water to granulate it, or the slag is removed after it has become solid and is broken up and reserved for re-treatment, to recover the tin it contains.

At intervals the reduced metallic tin is tapped from the bottom of the settler and is run into cast-iron molds. The pigs or slabs of tin are removed from the molds and are taken to the refinery for further treatment to remove the metallic impurities the tin contains.

Alexander[4] has proposed a modification of the blast-furnace smelting of tin concentrates in which the concentrates are first sintered with 7 to 10 per cent of coal. The sintering operation is said to remove 70 per cent of the sulphur and to leave the sintered material in the form of a cake that may easily be broken. The sintered material is fed into a blast furnace with coke and, if desired, some slag that must be resmelted for the tin it contains. The claim is made that, by using this process, slags low in tin and reduced metal low in impurities are obtained.

Smelting in Reverberatories.—The use of reverberatory furnaces for the smelting of tin concentrates dates back to the early part of the eighteenth century, when reverberatory tin-smelting furnaces were introduced into Cornwall. From that time on they came more and more into favor, until at the present time most of the modern

tin-smelting plants in various parts of the world use reverberatory furnaces, not only for the primary smelting of tin concentrates, but also for re-treating the first-run slags to remove the tin they contain.

By the use of reverberatory furnaces instead of blast furnaces it is possible to make somewhat cleaner slags in the original smelting of tin concentrates as well as in the resmelting of first-run slags, and the metallurgical operations are more readily controlled. Because tin is such a valuable metal, it is important to reduce the dust losses as much as possible. Reverberatory furnaces are particularly suited to the smelting of fine tin ores and concentrates, as the dust losses in reverberatory smelting are much less than in blast-furnace smelting.

FIG. 6.—Reverberatory tin-smelting furnace.

The reverberatory furnaces generally used for tin smelting are constructed of firebrick and vary greatly in size, the largest of them having a hearth about 30 to 40 ft. long and 12 to 15 ft. wide. They usually have the firebox at one end of the furnace and the flue at the opposite end. Long-flame bituminous coal usually is used for fuel, although oil is an excellent fuel for reverberatory smelting, and very satisfactory results may be obtained with it where the cost is not prohibitive.

The larger furnaces will take 8 to 15 tons of charge in each batch. The charge consists of tin concentrates with 15 to 20 per cent of anthracite screenings and small amounts of sand, limestone, slag, and refinery by-products. The charge is well mixed before it is fed to the furnace, and the process is a batch operation, a complete charge being fed to the furnace, smelted, and the furnace tapped before a second charge is put in. The proper temperature for operating tin reverberatory furnaces is 1200 to 1300°C. The larger furnaces usually require 10 to 12 hr. for each charge.

When smelting tin concentrates, a fairly large amount of tin is allowed to go into the slag, because it has been found that such practice tends to produce reduced metal containing a minimum amount of impurities and also a minimum amount of hard-head. The object is not so much to keep the tin out of the slag as it is to keep the impurities out of the reduced tin.

After a batch is smelted, it is tapped from the furnace through a single taphole, and the reduced metal and slag are allowed to run into a large brick-lined settler or forehearth. From the settler the slag usually overflows into cast-iron slag pots which are mounted on trucks and are drawn away on the slag track as soon as they are filled. To remove the slag from the pots the lower ends of bent iron bars sometimes are immersed in the slag while it is still molten, and after the slag solidifies it is lifted from the pots by means of these bars.

Slag obtained from the first smelting of tin concentrates contains so much tin that it must be resmelted, and after the slag cakes are removed from the pots they are broken up and crushed to pass about a ¾-in. ring. The crushed slag is transferred to slag-storage bins, where it is kept until required for slag-smelting charge. Reverberatory-furnace slags, obtained from the first-run smelting of tin concentrates, usually contain 10 to 25 per cent of tin.

The molten metallic tin is tapped from the bottom of the settler and is cast into pigs or thin flat slabs, weighing about 75 lb. each. The tin usually is cast in the form of slabs, as it has been found that the flat slabs are particularly suitable for charging to the refining furnace.

After the furnace has been tapped, the next charge is introduced immediately before the furnace has a chance to cool. Successful smelting requires that the charge shall be melted as quickly as possible so as to reduce the tin rapidly, which gives a high yield of clean tin. The charge is stirred at intervals with iron hoes attached to long iron handles which are operated through the side doors of the furnace. The stirring should be deep so as to remove any of the unsmelted charge that adheres to the bottom of the furnace. As soon as the appearance of the charge indicates that it is smelted completely, the charge should be tapped from the furnace.

Tin-smelting reverberatory furnaces are constructed of firebrick and have a fire-brick hearth sloping toward the taphole which usually is placed at about the center of one side of the furnace and low enough to drain the furnace completely when the taphole is open.

The roof is of arch construction, and, as in other reverberatory smelting furnaces, the roof should be sprung from and supported by heavy continuous steel-beam skew-backs, so that damage to the side walls will not endanger the roof, and side-wall repairs may be made without affecting the roof.

The furnaces usually are charged through several charge holes placed at regular intervals down the center of the furnace roof. The charge material often is kept in small feed bins located above the charge holes, each bin holding enough material for one or more charges, as desired.

Some of the tin compounds are somewhat volatile at the smelting temperatures, and even under the best conditions considerable tin passes out of the furnace in the form of fume and dust. Successful smelting operations require the use of dust-collecting equipment in connection with the smelting furnaces.

Slag Smelting.—Slag produced in the first-run smelting of tin concentrates, in either a blast or reverberatory furnace, as already said, invariably contains so much tin that it is necessary to re-treat it before it may be thrown away. First-run tin slag is re-treated in either a blast furnace or a reverberatory furnace of the same general type as is used for the smelting of tin concentrates.

The cost of smelting slag in a blast furnace is probably somewhat less than in a reverberatory furnace, but the second-run slag obtained from a blast furnace usually contains more tin than similar slag made in a reverberatory furnace.

In smelting slag the main object is to reduce to the metallic form the tin that is contained in the original first-run slag in the form of tin silicates. Generally speaking, a higher temperature is required for slag smelting than for the smelting of tin concentrates, because it is more difficult to reduce tin to the metallic form from the silicates of the slag than from the oxide in the concentrates.

A fairly large amount of reducing material is required in the smelting of slags, and when reverberatory furnaces are used, the reducing material usually is added to the charge in the form of anthracite screenings. Some limestone usually is added as a fluxing material. Sometimes metallic iron in the form of scrap or other readily obtainable material is added to the slag-smelting charge to replace the tin in the silicates of the slag and to permit the reduction of the tin to the metallic form. Lime sometimes is depended on to react with the tin silicates to bring about the same result. Metallic tin produced in the smelting of slags usually is impure and generally contains a large amount of iron in the form of hard-head tin-iron alloy.

The removal of tin from the first-run slag is one of the most difficult operations the tin metallurgist encounters, and successful slag smelting requires great care and expert control. Unless the slag-smelting operations are carefully conducted, the second-run slags will be high in tin.

In the best practice, the slag resulting from the slag smelting should not contain more than 1 per cent of tin, but second-run slags often contain more than 1 per cent of tin, and not infrequently slags containing 3 per cent or more are discarded.

Generally speaking, the metallic tin produced in the smelting of slag and also the metallic tin produced in the primary smelting of tin concentrates require some refining before they are ready for the market.

Some of the richer slags from the first smelting of tin concentrates, and also by-products from the refinery and from slag smelting, are returned to the tin-concentrate smelting furnace and are added to an original tin-concentrate smelting charge.

When reverberatory furnaces are used, 16 to 18 hr. is required for smelting a slag charge. Slag smelting in reverberatory furnaces is a batch process, the same as tin-concentrate smelting, an entire charge being smelted and tapped from the furnace before the next charge is put in. Reduced metal and slag are handled in settlers and slag pots in a manner similar to the handling of such materials from a tin-concentrate smelt. The slag is removed from the pots and is broken up and thrown away, or is poured over the dump while still molten.

Refining.—Most of the reduced tin obtained in the smelting of tin concentrates or slag must be refined before it is ready for the market. The tin obtained from the first smelting operation contains many metallic impurities that were reduced with the tin and are alloyed with it. The kind and the amount of impurities the tin contains depend largely on the metal impurities in the original tin concentrates, and, for that reason, the tin obtained from the smelting of some tin ores requires much more refining than does the tin from other ores.

Two methods of refining tin have been used extensively and successfully. In the first of these methods the tin is refined by heat-treatment, and in the second by electrolytic treatment.

The heat-treatment method is the one generally used in various parts of the world, and, although many modifications have been adopted in different places, tin is refined in substantially the same manner in the different localities.

The refining may consist of one or both of two operations: the first is liquating or sweating; and the second, boiling, tossing, or poling. Where both liquating and

boiling are necessary, the tin always is liquated first and is then subjected to the boiling treatment. Liquating is done in a comparatively small sloping-hearth reverberatory furnace built with the firebox at one end and the flue at the other. The hearth usually slopes to one side toward a large door or taphole, which discharges continuously into either one or two outside cast-iron kettles.

The object of liquation is to remove from the tin all metallic impurities, alloys, and compounds that have melting points appreciably higher than the melting point of tin, and by this process the tin is separated from the metallic impurities by liquating or sweating it at a temperature just slightly above its melting point.

The bars, pigs, or slabs of tin to be refined are placed on the upper side of the liquating-furnace hearth. The furnace is kept at a temperature just slightly above the melting point of tin, a slow fire being used for this purpose. Long-flame bituminous coal is used for fuel, and the temperature is carefully regulated.

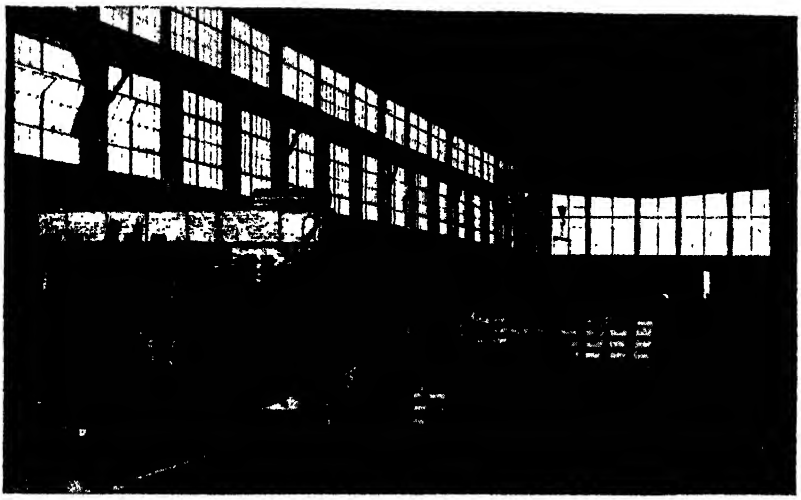

FIG. 7.—Liquating furnace with refining kettle.

The bars or slabs of tin are piled on each other with spaces between them, and the tin soon begins to melt and run down. The melting is slow, as the success of the operation depends on careful regulation of the temperature so as not to melt the metallic impurities that are present in the form of alloys and compounds associated with the tin.

The clean tin runs from the furnace into one of the outside kettles, leaving the residue on the hearth. After the metal that melts at a low temperature has been sweated out, the dross remaining in the furnace is pushed toward the fire and the temperature is raised until all possible metal has been removed. This second sweated metal is caught in the other kettle, as it is so impure that it should not be mixed with the metal obtained from the first sweat. The second metal is cast into pigs or slabs and is resweated with the next charge.

After the second metal has been sweated from the dross, the temperature is again raised and the dross is thoroughly roasted. The final roasted residue is resmelted with an original tin-concentrate charge in the tin-concentrate smelting furnace.

Many impurities are removed in the liquating furnace, but some of them which have comparatively low melting points are sweated out with the first sweat metal. Most of the iron is removed in the liquating furnace as it remains with the dross, but

a small amount goes into the sweated tin. Most of the lead and bismuth also go into the tin. Much of the arsenic, antimony, and copper remain with the dross.

The first sweat tin that collects in the cast-iron kettle outside the liquating furnace usually is boiled or tossed to complete the refining. The kettle holds 6 to 10 tons of metal and usually is separately heated by a coal fire underneath it. The metal in the kettle is heated to a temperature considerably above its melting point, and the boiling operation is carried on by stirring the molten metal with a pole of green wood or by immersing in it a bundle of green-wood sticks held together by iron bands. At the high temperature of the metal the green wood undergoes destructive distillation, and the steam and gases resulting from the distillation of the wood are given off beneath

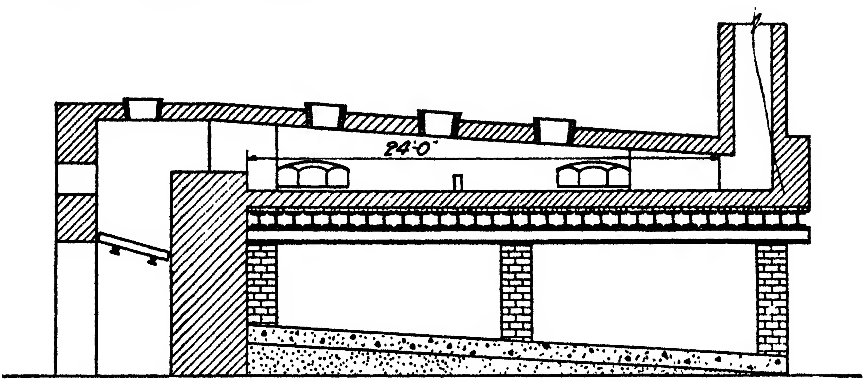

FIG. 8.—Sectional elevation of tin reverberatory.

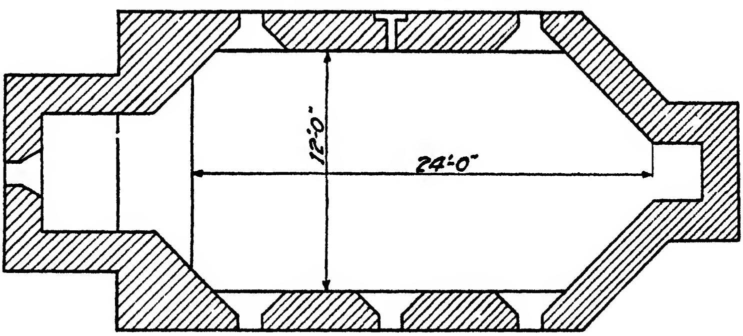

FIG. 9.—Sectional plan of tin reverberatory.

the surface of the metal and produce a strong boiling or bubbling action in the bath (*cf.* Copper Poling, page 253). In this way the different portions of the metal bath are brought to the surface and exposed to the air. Some of the metal impurities and part of the tin are oxidized, and the oxide drosses collect on the surface and are skimmed off from time to time. These drosses are resweated or are smelted with an original tin-concentrate smelting charge in the same way as the residues from the liquating furnace. In some of the more modern refineries, the boiling is done by agitating the molten metal with compressed air instead of green-wood sticks.

The boiling operation is carried on until the desired grade of refined metal is obtained. If the tin contains fairly large amounts of impurities, the boiling sometimes is continued for many hours. The metal must not be heated to an excessively high temperature, as boiling at a high temperature causes a large amount of the tin to become oxidized.

Tossing consists in filling hand ladles with the molten tin and pouring the molten metal back into the kettle, thus exposing it to the oxidizing action of the air. Tossing produces oxidized drosses similar to the drosses that form in the boiling operation. Boiling is the method usually used; both tossing and boiling are hardly ever employed at the same refinery.

Iron is removed almost completely by the boiling operation, and other impurities, principally arsenic and antimony, are greatly reduced in amount.

After the refining has been completed and the dross has been skimmed from the kettle, the surface of the metal will have a clean bright appearance, and the tin is then removed, usually by hand ladles, and is cast into pigs ready for the market. Great care is exercised in casting the pigs so as to give a fine appearance to the metal. Tin tends to oxidize on the surface while in the molten condition, and for that reason the metal is poured at a temperature just slightly above its melting point. The metal is poured into cast-iron molds, which are filled quickly and are skimmed lightly on the surface with a wooden paddle just before the metal solidifies.

Electrolytic Refining of Tin.—This process has been used successfully at one refinery in the United States, but, because of economic conditions previously discussed in this book, tin smelting and refining in the United States were abandoned in 1923, and since the closing of this American electrolytic-tin refinery, the electrolytic-refining process no longer has been used to any extent for the treatment of tin from primary ores.

As in the electrolytic refining of other metals, many impurities originally contained in the tin are removed by this process, and very pure tin is produced. Because of the possibility of removing the metallic impurities from the tin, it is not so essential, when electrolytic refining is to follow the smelting operation, to remove the other metal minerals from the tin concentrates before smelting. The refining is carried on in the usual way in electrolytic cells, tin being deposited on the cathode and minor amounts of other metals being recovered in the form of anode slime by-products. The patents state that, as originally developed, the electrolytic tin-refining process made use of an electrolyte of hydrofluosilicic acid containing sufficient sulphuric acid to combine with the lead present to form lead sulphate. In the later modification of the electrolytic-refining process, the electrolyte consisted of hydrofluosilicic acid containing some sulphuric acid, a small amount of cresylic acid, and glue. The hydrofluosilicic acid used was of about 15 per cent strength and had about 4 per cent of tin dissolved in it.

Vail[5] states that, at the American refinery where this process was used, the refining was done in 68 tanks similar in size and construction to those used for copper refining. The tanks were of wooden construction and were lined with asphaltic material. Hard-rubber fittings were used for the pipe lines which carried the electrolyte. Each tank contained about 11,000 lb. of tin anodes, and the cathode starting sheets were of tin ⅛ in. thick. The current density was about 12 amp. per sq. ft., and the deposition per ampere-hour was about double that of copper. Vail also states that, before being cast into anodes, the tin obtained from the smelting of tin concentrates was first subjected to refining by liquating and boiling. A general description of the process is given in the patent specifications[6].

Methods of Assay and Analysis.—There are two general methods in use for determining the amount of tin in ores and other products: the fire assay and the volumetric wet analysis.

The fire assay for tin usually is conducted in the following manner: Grind slightly more than 5 g. of the sample until it will pass through a 100-mesh screen. Dry at 100°C. and cool; weigh out exactly 5 g. into an 8-oz. wide-mouthed flask. Add 100 cc. hydrochloric acid (concentrated), and digest at a low heat until the volume is

reduced to about 15 cc. Add 50 cc. nitric acid (concentrated), and continue the evaporation to a volume of 10 to 15 cc. Add about 200 cc. of water, boil, and allow to stand. Filter on double filter papers containing paper pulp, washing with warm water just acid with nitric acid. If tungsten is present, treat with ammonia (concentrated) and again filter and wash with water. Transfer the precipitate to a porcelain crucible and ignite. Brush the contents of the crucible onto a clean sheet of glazed paper, break up lumps with a spatula, mix thoroughly with 20 g. of sodium cyanide (free from chlorides), and transfer to a 20-g. clay crucible in which has been placed 4 or 5 g. of sodium cyanide. Cover with sodium cyanide, fuse in a muffle furnace at a red heat for 20 to 25 min., cool wash with water, break the crucible to obtain the button, clean the button, and soak in hot water to remove adhering cyanide. Dry and weigh. Run in duplicate. Duplicates should agree within 0.15 per cent.

The volumetric determination of tin is very useful and is applicable to nearly all kinds of ores, metallurgical products, and other materials containing tin. A number of volumetric methods have been proposed, the best of which depends on the titration of stannous chloride with standard iodine in cold hydrochloric acid solution. This is called the Pearce-Low method[7], and is one of the simplest, shortest, and most accurate for the volumetric estimation of tin. It depends on the oxidation of stannous to stannic chloride by iodine in cold hydrochloric acid solution according to the equation

$$SnCl_2 + 2HCl + I_2 = SnCl_4 + 2HI$$

Starch solution is used as indicator. A small amount of sulphuric acid is not objectionable, but nitric acid and nitrates must not be present.

The method requires that the tin shall be brought into solution in hydrochloric acid. When possible, the finely ground sample is dissolved directly in hydrochloric acid; in some cases the addition of a small quantity of potassium chlorate, antimony chloride, or platinic chloride, or the presence of a piece of platinum foil, accelerates solution. In the analysis of materials containing sulphides or certain alloys, a mixture of hydrochloric and nitric acids may be used, followed by treatment with sulphuric acid and then with hydrochloric acid. Siliceous products frequently respond to treatment with hydrofluoric acid.

For the decomposition of insoluble silicates, fusion with alkali carbonates is effective. Practically all silicates are decomposed by this process, but it is not suitable for use with samples containing insoluble tin oxide, and if sulphides or salts of tin soluble in acids are present they should be removed before the fusion process is applied. The addition of 10 per cent of borax to the alkali carbonate accelerates the decomposition in some instances.

Acid-insoluble residues may be decomposed by fusion with sodium or potassium hydroxide, the melt being subsequently dissolved in hydrochloric acid. This method is perhaps the most useful of the fusion processes, since it is applicable to almost all products and generally requires only a very simple preliminary acid treatment. An iron crucible is the most suitable for use with this process.

Sodium peroxide also may be used for the fusion process, but it corrodes the crucibles very rapidly, and generally its disadvantages more than offset the extra speed gained by its use. The addition of organic matter to the peroxide, to furnish the necessary heat for the reaction, has been suggested as a means of preventing the corrosion. Quieter fusion results if zinc sulphide, iron sulphide, or potassium persulphate is added to the peroxide.

In the final hydrochloric acid solution, the tin usually will be found in the stannic condition and must be reduced to the stannous condition before titration. This reduction usually is accomplished in one of four ways: by the use of iron in the form of

rods, nickel or aluminum in the form of sheets or strips, or finely powdered antimony. Only pure soft iron may be used. If carbon is present in the iron, it generally will cause high results.

The use of aluminum renders this part of the method somewhat uncertain and makes it difficult to control the operation. The principal objection to the use of antimony is that the presence of so much finely powdered material in the solution obscures the end point. The only objection to nickel is the light-green color given the solution, but this does not affect the sensitiveness of the end point if the concentration of nickel salts is only that derived from the metal used for the reduction.

The reduction and the titration are best performed in an atmosphere of carbon dioxide and in a solution containing not less than 25 per cent nor more than 40 per cent by volume of free concentrated hydrochloric acid. The temperature of the solution to be titrated should not exceed 22°C.

One-half to 2 g. of the sample (depending on the percentage of tin) is first brought into hydrochloric acid solution. The solution is transferred to a 12-oz. wide-mouthed conical flask, enough concentrated hydrochloric acid is added to make a total of 50 cc. of free concentrated hydrochloric acid present, and the solution is diluted to 200 cc. with water. A nickel coil is prepared by rolling 6 sq. in. of heavy sheet nickel (4 in. long and 1½ in. wide) into a loose roll of such size that it may easily be inserted into the flask. A narrow strip of nickel is left attached to one side of the coil, long enough to reach above the top of the flask. This coil is placed in the flask containing the tin solution, the nickel strip is bent over the edge, and the flask is covered with a small watch glass. The solution is heated to boiling, and gentle ebullition is maintained for 30 min. after all the iron which is present is reduced. The reduction of the iron is indicated by the yellow color of the solution changing to a pale green. Thirty minutes is more time than is necessary for the complete reduction of the stannic chloride from 0.5 g. of tin oxide, and if complete reduction does not result in that length of time either the nickel is too small or the nickel is inactive, due to impurities, and should be discarded and replaced by pure nickel.

It has been stated, as an objection to this method, that it is impossible to tell when the reduction of the tin is complete and that the operator may titrate the solution before the tin is all in the lower form. It has been found that larger amounts of tin than would ever be taken as a sample are entirely reduced long before the expiration of the time allowed for the reduction, and no trouble need be anticipated from this cause.

The solution in the flask is cooled in an atmosphere of carbon dioxide generated by adding two ½-in. cubes of crystalline marble to the solution. The nickel coil is then removed and is washed with cold hydrochloric acid solution (1 part of concentrated acid to 3 parts of water) as it is withdrawn from the flask. A small amount of starch solution is then added and the solution titrated at once with standard iodine.

The standard iodine solution most convenient for this titration is prepared by dissolving 10.7 g. of iodine in 50 cc. of water containing 20 g. of potassium iodide in solution and making up to 1 l. with water. When a ½-g. sample is taken for analysis, 1 cc. of this solution will equal 1 per cent of tin. It may be standardized against tin or arsenious oxide.

Few of the elements that are ordinarily found in materials to be analyzed for tin interfere with this method. Ni, Co, Mn, Mo, U, Cr, Al, Zn, Pb, Ca, Mg, sulphates, phosphates, bromides, iodides, and fluorides have no effect unless present in such large amount that their color masks that of the indicator. Arsenious and antimonious compounds in weak acid solution consume iodine, but in a hydrochloric acid solution of the strength used in this method they have no effect.

If about 0.1 g. or more of antimony is present in the solution, the nickel coil will precipitate metallic antimony in a very slimy condition which does not settle and obscures the end point. This may be prevented by using a solution containing more hydrochloric acid. If, therefore, the sample taken contains 0.1 g. or more of antimony, the solution is made up to contain 75 cc. of free concentrated hydrochloric acid instead of 50 in 200 cc. of volume, before reduction. If this is done, the precipitation of slimy antimony will be prevented and no trouble will be experienced. If the antimony content is not known and the slimy antimony begins to precipitate during the reduction, an additional 25 cc. of concentrated hydrochloric acid may be added, which generally will cause the antimony to dissolve and prevent further precipitation. If the precipitated antimony does not dissolve, another sample can be treated, adding more hydrochloric acid before reduction.

Copper in small amounts has no effect on the method, but if 0.05 g. or more is present in the solution it will be precipitated incompletely during the reduction, the titration will consume more iodine than is required by the tin, cuprous iodide will be precipitated, and the results will be erratic and high.

If copper is present in the sample in large enough amount to interfere, it must first be removed by treatment with nitric acid.

Bismuth is precipitated in the metallic form during the reduction with nickel. In this form it is said to consume iodine slowly, but the action is slight, and unless present in large amount, its effect is negligible. If it is desired to remove it, the metallic precipitate may be filtered and the filtrate again reduced and finished as usual.

Tungsten is reduced by the nickel coil to a lower state of oxidation, with the formation of a blue precipitate, said to be W_2O_5. This is said to be oxidized slowly by iodine, thus giving high results, but the oxidation is not proportional to the amount of tungsten present. Tungsten in amounts usually met with does not interfere to any extent, and its effect is noticeable only when it is present in large quantity. In case it should be desirable to separate the tungsten, the blue oxide may be filtered off with the precipitated bismuth, the solution afterwards being again reduced and titrated.

Titanic chloride is reduced to titanous chloride by the nickel coil. In the Pearce-Low method titanium alone or with iron is said to consume no iodine, but in the presence of tin large amounts of titanium will consume iodine, giving high results. The error caused by titanium seems to be approximately a constant one and is independent of the amount of titanium present. Titanium may best be removed by converting the tin to insoluble oxide by evaporation with nitric acid and then fusing for 5 min. with potassium bisulphate. The melt is dissolved in water and sulphuric acid and filtered.

If titanium and tungsten are both present, the tungsten will remain with the tin after filtering the extracted melt of the bisulphate fusion. The tungsten may be removed from the residue by heating with ammonium carbonate solution, in which the tin is insoluble.

Bismuth, tungsten, or titanium, in any reasonable amount, such as is usually met with, do not interfere with the method, and they may, in general, be neglected. especially if the titration is performed rapidly, which, to a large extent, will eliminate secondary reactions. The interference of all these metals is greatly increased by very slow and careful titration, which seems to accelerate their action and give them time seriously to affect the results. This is especially true of titanium, for bismuth and tungsten are not so active and, as a rule, need not be considered.

Ferrous chloride is oxidized only by excess of iodine, and no action takes place unless a very large amount of iodine is run in and allowed to stand. Its action is very slow even then, and the presence of iron does not affect the accuracy of this method.

A tin determination may be run through and results obtained by this method in about 1½ hr., and the method is accurate to about 0.1 per cent.

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CHAPTER XXV

MINOR AND RARE METALS

BY DONALD M. LIDDELL

Be (4), Ct (72), Ce (58), Cb (41), Dy (66), Er (68), Eu (63), Gd (64), Ga (31), Ge (32), Hf (72), Ho (67), In (49), La (57), Lu (71), Ma (43), Mo (42), Nd (60), Pr (59), Rb (37), Re (75), Sm (62), Sc (21), Se (34), Ta (73), Te (52), Tb (65), Tl (81), Th (90), Tm (69), Ti (22), Yb (70), Y (39), Zr (40). (The figures in parentheses are the atomic numbers. The true rare-earth metals have the 15 atomic numbers from 57 to 71. In these elements, the four-quantum shell expands from 18 to 32 without change in the outer shells 5 and 6. The fact that there is only this slight progressive difference in molecular structure is what makes their properties so similar and their separation so difficult.)

General Considerations.—The final separation of the rare earths usually depends on repeated fractional crystallizations or precipitations and leachings. The separations are not clear cut, and the spectroscope is the final method of test for purity. The work with the rare metals and earths therefore requires an immense amount of time and patience.

One general separation of the entire group depends on the fact that when tartaric acid, ammonia, and ammonium sulphide are added to the filtrate from the H_2S group Fe, Zn, Co, Cr, Ni, V, Al, and Mn will be precipitated (the last two not quite completely) and in the solution will remain W, Ti, Zr, Th, Be, Ca, Mg, Na, K, Li, traces of Al, and Mn, and the rare earths.[1]

From this solution, precipitation with oxalates in acid solution, re-solution, and reprecipitation will give only the rare earths in the final residue.

Hopkins gives the following general procedure:[2] The ore is ground to a fine powder and extracted with acid or fused. The acid is usually HCl or H_2SO_4, although HF is sometimes employed. The fusion mixture may be $HKSO_4$, NaOH, or HKF_2. The use of the fluorides is usually limited to minerals containing columbium and tantalum, since the fluorides of these compounds are soluble and hence can be separated from the insoluble fluorides of the rare earths, which can then be decomposed with H_2SO_4.

The solution is saturated with hydrogen sulphide to throw out the copper-tin group and the rare earths then thrown down with oxalic acid. Both solutions should be boiling and the oxalic acid added slowly.

Thorium and zirconium can be removed by boiling the crude oxalates with ammonium oxalate, which dissolves all the zirconium and most of the thorium. Thorium may be completely removed by repeated treatments with ammonium oxalate, or by precipitation from a neutral or slightly acid solution with H_2O_2.

Columbium and tantalum, if present, are also removed by this means.

The rare-earth oxalates remaining after extraction of the Cb, Ta, Zr, and Th are then separated into the cerium-group earths and the yttrium-group earths. James' method is as follows: Mix the dried oxalates with enough sulphuric acid to form a thick paste, then ignite cautiously. Dissolve the anhydrous sulphates in ice water and

[1] *Jour. Chem. Soc.*, Vol. 119, 1927.

[2] "Chemistry of the Rarer Elements," p. 98.

sift in solid sodium sulphate. The order of precipitation is, approximately, Sc, La, Ce, Pr, Nd, Sm (the cerium group, sulphates difficulty soluble); Eu, Gd, Tb (terbium group, sulphates slightly soluble); Yt, Dy, Ho, Er, Tm, Yb, Lu (yttrium group, double sulphates very soluble). The separation is not exact, and the yttrium group will begin to come down before all the cerium group is precipitated. Consequently, to obtain the cerium group free from the yttrium group, much of the former must be left in solution. To obtain the yttrium group free from cerium, enough alkali sulphate

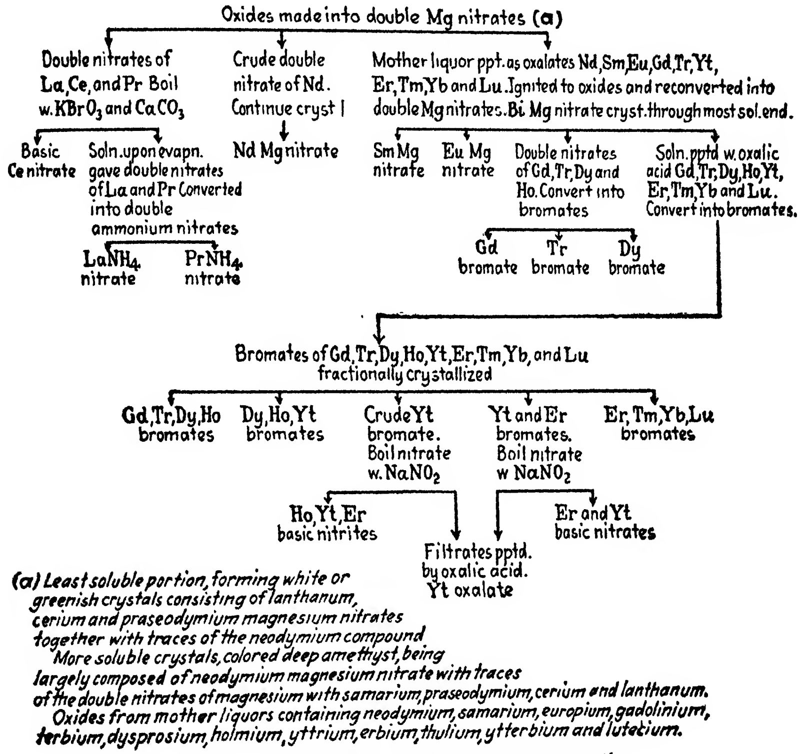

FIG. 1.—Flow sheet of precipitating rare earths.

must be added to precipitate a considerable amount of the yttrium group. If the purification of any members of the yttrium group is purposed, it is best to add alkali sulphate until the neodymium absorption lines can no longer be seen.

Cerium itself may be removed by the treatment of a neutral solution with potassium bromate and a few small pieces of limestone. The cerous salts are oxidized to ceric and come down as a basic precipitate.

The cerium-earth double sulphates can be reduced by fusion with charcoal and will then go into solution with hydrochloric acid.

Cerium can also be removed by the James bromate method.[1] In this some small pieces of lime are added to the nitrate solution, to keep it neutral, and then $KBrO_3$ is added and the solution boiled. The cerium is oxidized to the quadrivalent condition and precipitates as a basic salt.

If the crude oxalates from the mineral contain less than 20 per cent of the yttrium group, it is well to begin fractional crystallization of the nitrates at once. When the

[1] JAMES and PRATT, *Jour. Am. Chem. Soc.*, Vol. 33, p. 1326.

yttrium elements in the soluble end of the series become abundant enough to interfere with the crystallization of the cerium group, then the cerium group should be separated with sodium sulphate.

Except for these few general methods, the separations are long-continued fractional crystallizations or precipitations. Urbain and Welsbach sometimes made thousands of crystallizations in the effort to differentiate two of these rare earths. The process of fractional crystallization is very well described by Dr. Doerner under Radium (see page 645). A table of comparative solubilities appears below, and James and Pratt's scheme appears on page 681.[1]

In the more soluble end of the crystallizations it may be necessary at some time to throw down the rare earths as oxalates to get rid of accumulated iron and alumina.

COMPARATIVE SOLUBILITIES
(The solubility increases from top to bottom.)

Double Mg nitrates	Bromates	Double sulphates	Sodium glycolates	Fused nitrates	Dimethyl phosphates[2]
La	La	Sc	Yt	Ho	Yb
Ce	Ce	La	La	Tb	Er
Pr	Pr	Ce	Ce	Sm	Yt
Nd	Nd	Pr	Pr	Gd	Gd
Sm	Sm	Nd	Nd	Eu	Sm
Bi	Bi	Sm	Sm	Yt	Nd
Eu	Eu	Eu	Gd[1]		Pr
Gd	Gd	Gd			Ce
Er	Tb	Tb			La
Yt	Dy	Dy			
Tm	Ho	Ho			
Lu	Yt	Er			
Ho	Er	Tm			
Dy	Tm	Yt			
Tb	Ny	Yb			
	Lu	Lu			
	Ct				
	Sc				

[1] *Solubility about twice the Sm salt.*
[2] *The double dimethyl phosphates are much less soluble at 80 or 90°C. than at 15 to 20°C.*

The preparation of the double magnesium nitrates, which are very useful in fractional crystallizations, is carried on as follows: The rare-earth oxides are dissolved in nitric acid, having a slight excess of the oxides present, and then the solution is reduced (chiefly ceric to cerous salts) by means of a little of the original oxalates from which the oxides were derived. A quantity of nitric acid equal to that in which the oxides were dissolved is then neutralized with chemically pure magnesium oxide, and the rare-earth and the magnesium solutions are then filtered and added together.

Basic nitrates can be made in two ways. The first method consists in converting oxalates into oxides, thence to nitrates, recovering the nitrate as a solid salt, and fusing until decomposition sets in. In dissolving the resultant mass with water the solubility runs: Yt, Eu, Gd, Sa, Tb, Ho, the holmium salts being least soluble.

[1] Reprinted from *Jour. Am. Chem. Soc.*, 1916, p. 43.

The second method consists in adding hot caustic soda little by little to a boiling solution of the nitrates.

In general, crystallization should be carried on by two methods used alternately, one of which tends to concentrate the impurities in the crystals and the other in the mother liquors.

Aldebaranium, cassiopeium, denebium, dubhium, and neothulium were the names given to elements that Auer von Welsbach separated from erbium, which he regarded as of complex nature, and from thulium. Later investigators have not confirmed his findings.[1]

Beryllium.—For the extraction of beryllium from beryl, H. Copaux suggests the following:[2] Heat the mineral with two parts of Na_2SiF_6, forming Na_3AlF_6 and Na_2BeF_4. Crushing followed by lixiviation removes most of the Be with a little Al. BeO, Al_2O_3, and SiO_2 are then thrown down with boiling NaOH, dissolved in H_2SO_4, and pure $BeSO_4.4H_2O$ crystallized out. Cb and Ta interfere and must be removed as oxalates. (See page 67 also.)

The separation of beryllium from the other iron-group metals can also be carried out by fusing with sodium carbonate. Al_2O_3 and Cr_2O_3 form soluble compounds that can be leached out. Fe_2O_3, TiO_2, ZrO_2, and BeO stay behind. A fusion with $HKSO_4$ then separates the iron and beryllium. While recommended for large-scale use it seems a laboratory method.

The preparation of beryllium from gadolinite is thus described by James.[3] The finely powdered mineral is treated with hot H_2SO_4 to dense fumes. The solution is allowed to settle, is decanted, and hot oxalic acid solution added. After filtering off the rare-earth oxalates, $KBrO_3$ is added to oxidize the oxalic acid, and iron and beryllium precipitated together by adding a little ammonia, then sodium hydroxide, until the odor of ammonia is noticed. Filter. Enough hydrochloric or sulphuric acid is then added to dissolve about two-thirds of the precipitate, and sodium hydrate slowly added until the iron is almost down (as shown by testing a clear portion of the solution) and the solution filtered. The remainder of the iron is then treated with hypobromite solution at boiling, and precipitated with sodium hydroxide until ammonia gives a white hydroxide precipitate with it. The last trace of iron is then thrown out with sodium-hydrogen sulphide and filtered off. (These last two residues contain beryllium and are worked up with the next lots of mineral.) The beryllium is then thrown down as basic carbonate by adding a concentrated solution of sodium carbonate to the solution. The hydrogen sulphide must be boiled out before this precipitation.

Beryllium has been obtained as metal by reduction of the chloride by sodium and potassium, in an atmosphere of hydrogen. Another process is to heat beryllium potassium fluoride with sodium. It has been obtained in lustrous hexagonal crystals by electrolyzing the double fluoride of beryllium and sodium or potassium with an excess of beryllium fluoride. A more recent process electrolyzes a fused bath of sodium and beryllium fluorides with an output of compact metallic beryllium. The metal is 99.6 per cent pure.

It has a silvery luster and when cold flattens easily under the hammer. The specific gravity is 1.79 and the melting point 1385°C. The metal is insoluble in cold concentrated nitric acid. Its specific heat is 0.4070.

About 0.5 per cent of beryllium is added to the thorium-cerium solution used in incandescent gas mantles to give body to the mantle.

Cassiopeium.—See Aldebaranium.

[1] *Sitzb. Akad. Wiss.* (Vienna), Vol. 2, *a*, p. 124; *Jour. Chem. Soc.*, Vol. 110 (II), p. 277.
[2] *Chim. Ind.*, Vol. 2, p. 914, 1919.
[3] *Jour. Am. Chem. Soc.*, Vol. 38, p. 875.

Celtium (Ct).—Reported by G. Urbain in 1911 as allied to lutecium and scandium. In properties it lies between them. Now known as hafnium (*q.v.*).

Cerium.—Except for the pyrophoric alloys and cerium steels (these showing no great advantage over cheaper alloys), this metal has no metallurgical applications. There is a steady economic pressure from thousands of tons of accumulated residues in the gas-mantle industry, but no absorption into the arts. While this is due to its price, this could not be permanently lowered because of a true scarcity of cerium in the earth's crust, and any considerable use would immediately reduce supplies to the vanishing point.

Lanthanum, praseodymium, neodymium, and samarium are the related elements.

Metallic cerium cannot be obtained by electrolysis of the fused salts, except in finely divided condition. Escard[1] recommends electrolyzing a mixture of 3 parts $BaCl_2$, 3 parts CaF_2, 8 parts $CaCl_2$, and 10 parts $CeCl_4$, heating the mixture in an electric furnace and using an iron crucible as cathode. $CeCl_4$ is added as the reaction proceeds. At 200 amp. and 15 volts he says a product results containing 98 per cent cerium, 1 per cent iron, and traces of oxide and carbide. The metal can be purified by amalgamation and distillation of the mercury. It has a density of 6.78 and a melting point of 775°C. It is only slowly affected by cold water, but rapidly by hot water, with the evolution of hydrogen. It burns when heated to 160°C. The pyrophoric alloys cerium-magnesium and cerium-aluminum can be obtained by simultaneous electrolysis of the mixed salts. Cerium-iron may be obtained in the absence of air by heating the elements in an electric furnace in a graphite crucible at red heat —cerium 70 per cent, iron 30 per cent, is the common alloy.

Metallic cerium cannot be obtained by reduction of the oxide by carbon, as a carbide forms, even in the presence of an excess of the oxide, in which case $CeC_2.2CeO_2$ is formed. Formation of the carbide may be prevented by adding CuO, copper-cerium alloys being formed.

The initial separation of the metal from monazite sand is by dissolving the sand in sulphuric acid and adding $HNaSO_4$ to throw down double sulphates of cerium-group metals and sodium.[2] It can also be separated as a phosphate as follows: Monazite sand is treated with concentrated sulphuric acid and carried to fumes. The soluble salts are then extracted with cold water. If the extract carries less than 5.8 per cent of $Ce_2(SO_4)_3$, the sulphuric acid should be brought up to 12 per cent. If the cerium sulphate runs between 5.8 and 11.5 per cent, the free sulphuric acid should be brought up to 20 per cent; if there is over $11\frac{1}{2}$ per cent of $Ce_2(SO_4)_3$, the free sulphuric acid should be brought up to 25 per cent. The solution is then oxidized for 8 hr., using a platinum gauze or a peroxidized lead anode and a platinum cathode. The cathode current should be 1.2 amp. per sq. dm.; the anode current density should be 1 amp. per sq. dm. By diluting to 10 per cent sulphuric acid in the presence of phosphoric acid, about 99 per cent of the cerium is precipitated.

Metallic cerium can be precipitated by the electrolysis of a fused mixture of 22 per cent sodium chloride, 15 per cent potassium chloride, and 63 per cent cerous chloride.

In the formation of cerium carbide in the electric furnace the process seems to be a three-stage affair:

$$2CeO_2 + C = Ce_2O_3 + CO$$
$$C_2O_3 + 9C = 2CeC_3 + 3CO$$

and the CeC_3 then breaks down into CeC_2 and graphite, so that it seems impossible to prepare CeC_2 without graphite.[3]

[1] *Ind. chim.*, Vol. 5, p. 182.

[2] U. S. patent 1279257, W. S. Chase.

[3] DAMIENS, A., *Ann. chim.*, Vol. 10, p. 330.

Sebacic acid in boiling aqueous solution precipitates thorium quantitatively, but not cerium or lanthanum. By the addition of bromine water in excess to a suspension of the cerium earths in alkaline solution, followed by heating at 100°C. until the excess bromine is expelled, and then filtering, the filtrate will be freed from cerium and will contain lanthanum and didymium.

Waste material from the gas-mantle industry can be used for the preparation of metallic cerium.[1] The oxides are dissolved in HCl, using an excess of oxides. Sodium and phosphorus compounds are removed with barium chloride and iron, manganese, and chromium by ceric oxide. The solution is then evaporated. The formation of oxychlorides is prevented either by an atmosphere of HCl gas, or by 30 per cent by weight of a mixture of KCl and NH_4Cl, or NaCl and NH_4Cl is added before evaporation. After evaporation, fusion is effected in cast-iron pots high in carbon and silicon, and the fused salt boiled for 20 min. The mixture is then transferred to the electrolytic cell and electrolyzed at 850°C., with an anode current density of 6 to 7 amp. per sq. in. for graphite and 5.5 amp. for carbon. About 7 to 12 volts pressure is used. If the electrolyte was prepared by the second method, the temperature may be raised to 950°. After the twenty-fourth hour, heat and stir every half hour to agglomerate the cerium, shutting down at the end of about 27 hr. If the electrolyte was prepared by the second method, the process may run 60 hr. The pot that served for the electrolysis is broken up, as it is too much attacked to use again. There are small quantities of lanthanum, dysprosium, erbium, and thorium in the cerium thus produced.

Misch metal can be prepared from the gas-mantle residues without purification. This will ordinarily run 50 to 60 per cent Ce; 25 per cent La; 15 per cent Dy, Sa, etc.; and 1 to 2 per cent Fe.[2]

About 0.3 to 2.0 per cent CeO_2 is recommended in the ThO_2 for gas mantles.

Crude cerium oxalate gives up its iron impurities upon treatment with dilute hydrochloric acid. It can then be converted to hydrate by boiling with KOH or to oxide by calcination. Pure CeO_2 appears to be of a light chamois color.

Columbium.—The element, in the form of oxide, is almost invariably associated with tantalum ores, its separation from tantalum being described under the discussion of that metal. The columbium remains in solution as potassium fluoxycolumbate ($2KF.NbOF_3$).

Columbium can be separated from zirconium by fusion with sodium carbonate and leaching with hot water. Columbium dissolves completely, tantalum largely, zirconium not at all.

Metallic columbium can be prepared by electrolysis of the molten fluocolumbate, prepared as given under Tantalum (*q.v.*).

The alloys of columbium are said to be highly acid-resistant, two in particular being noted: Zr, 6.8; Cb, 53.5; and Ta, 39.7 per cent (Canadian patent 214118); and Ni, 75; Fe, 11; and Ta and Cb, 14 per cent.[3]

Denebium.—See Aldebaranium.

Dubhium.—See Aldebaranium.

Dysprosium.—This metal was discovered in 1886 by Lecoq de Boisbaudran, who named it for the Greek "difficult to approach," because of the trouble he had in isolating it. The mineral or residue is decomposed with hydrochloric acid, the rare earths precipitated as oxalates, and the precipitate washed to remove iron and

[1] British patent 119229 of 1918.

[2] A historical review by B. Simmersbach of pyrophoric alloys will be found in *Chem. Z.*, Vol. 45, p. 577, 1921.

[3] A good reference for the analytical chemistry of columbium is MOIR, J., *Jour. Chem., Met. Soc. S. Africa*, Vol. 16, p. 189. A brief outline will be found in JOHNSTONE's "Rare-earth Industry," p. 60, D. Appleton. For a general discussion of columbium, see, Balke, *Ind. Eng. Chem.*, Vol. 27, pp. 1166–1169, October, 1935.

beryllium. Usually the earths are reprecipitated to remove silicon and iron further. If the cerium group is present, it is best removed by the double-sulphate method. In this, the oxalates are converted to sulphates by moistening with sulphuric acid and ignition to 400°C.; the resulting sulphates dissolved and solid sodium or potassium sulphate added to the solution to saturation (see page 680), most of the cerium group being thrown down in such a solution. The earths in solution should then again be precipitated as oxalates to get rid of the alkali salts. Specific gravity is 8.44.

As the yttrium group are again in solution as sulphates, the metals are converted to bromates by double decomposition with barium bromate. The bromates are then recrystallized fractionally.

Least Soluble	Middle	Most Soluble
Sm, Nd, Pr	Dy, Ho	Er, Yt, Tm

The recrystallization of these salts as double ethyl-sulphates is also practiced, the oxides being converted into the double salts by prolonged agitation with ethyl sulphuric acid. In this case absolute alcohol is used as the solvent and the fractionation takes place at 9°C., the resolution of the crystallized portions being performed at 30 to 40°C. In order of increasing solubilities: Gd, Tb, Nd, Pr, Ho, Dy, Y, Er, Yb. The first three are readily removed from dysprosium, but holmium is not.

Xenthotime and gadolinite are the main sources of dysprosium.[1] The closely related elements are erbium, holmium, and thulium.

Erbium.—This metal is derived mainly from gadolinite. The generally followed method of extraction is that given on page 683. The main difficulty is in its separation from europium and gadolinium. Wichers, Hopkins, and Balke[2] say that fractional precipitation of the cobalticyanides or with sodium nitrite gives good results, but that the classic nitrate fusion (fractional decomposition) is best. Willard and James recommend the sodium nitrite method for work on a large scale. See also under Dysprosium.

Europium.—This metal is obtained from monazite sand residues. It was identified in 1901 by Demarçay, who found he was working with a nitrate more soluble than gadolinium and less soluble than samarium. Its salts are a pale rose color. Specific gravity is 5.30.

The eventual separation is best performed by fractional crystallization of the double-magnesium nitrates, using 30 per cent HNO_3 as the solvent (see page 682 for solubilities). The separation of samarium from europium is finally accomplished by adding some bismuth-magnesium nitrate to the solution. The bismuth-magnesium nitrate has a solubility lying between samarium and europium. The bismuth with which each fraction is contaminated is finally thrown out by hydrogen sulphide.

Europium and ytterbium are said to be unique among the rare earths in giving amalgams if solutions of the acetates in tertiary potassium citrate are stirred with potassium amalgam. (*Jour. Am. Chem. Soc.*, Vol. 63, p. 3432.) The electrolysis of the above solutions when electrolyzed with a mercury cathode is also said to give Eu and Yb amalgams. The elements most closely related to europium are gadolinium and terbium.

Florentium.—Dr. Rolla, of the University of Florence, Italy, proposed this name for what appears to be illinium (element 61).

Gadolinium.—This metal was identified in 1880 by C. Marignac in samarskite It is named for the mineral gadolinite, which, in turn, is named for the Finnish

[1] For a general discussion of dysprosium see *Jour. Am. Chem. Soc.*, Vol. 39, p. 53, and Vol. 40, p. 593.

[2] *Jour. Am. Chem. Soc.*, Vol. 40, p. 1615.

chemist, Johann Gadolin. It is now chiefly obtained from monazite sand residues.[1]

Crystallization of alkali-gadolinium sulphate and hydrazine-gadolinium double sulphate gives only a rough concentration of gadolinium. Crystallization of the bromates gives a good method for separating the terbium earths from the yttrium group, but does not separate the terbium and cerium groups. The acetate method gives a good separation of Gd from Sa, Pr, and Nd.

Compound	H_2O of crystallization	Grams salt in 100 g. of saturated soluble at 25°C.
Lanthanum acetate	1.5	14.47
Praseodymium acetate	1.0	21.48
Neodymium acetate	1.0	20.76
Samarium acetate	3.0	13.05
Gadolinium acetate	4.0	10.37
Yttrium acetate	4.0	8.28

Double nitrates of bismuth and these earths fractionate in the reverse of the acetates, and alternated with the acetate method, give a good separation. Fractional crystallization of the nitrates gives a rapid separation of the cerium earths in the early stages, but toward the end is much inferior to the acetate. Gadolinium can be rapidly separated from terbium by fractional precipitation with NH_4OH.[2]

If a mixture of sulphates is reduced by strontium amalgam, Gd can then be quickly separated from Tb, Y, Sm, and Eu by precipitating the gadolinium as a benzene sulphonate.

Gallium is found chiefly in the flue dusts of zinc works. During the First World War, when large quantities of zinc were redistilled, residues were left comparatively rich in gallium and indium. This alloy is volatile at the temperature of the ore furnace, but resists distillation for weeks at 1000°C.

It is probable, according to G. W. Waring, that any practical method of extraction must be founded on fuming the ore at a high temperature, *circa* 1500°C., and separating the gallium from the flue dusts or where redistillation of spelter is carried on, on a tremendous scale. Gallium is interesting because of its low melting point, 30.8°C., and high boiling point. It instantly spreads in a thin mirror film over any sort of a dry surface (it wets glass), and it re-collects in a globule when wet with slightly acidulated water. The metal undercools after melting and may not solidify until 0°C. is almost reached.

Gallium may be separated from iron by the solubility of its hydroxide in NaOH, and from aluminum and chromium by precipitation as ferrocyanide. The ferrocyanide, $Ga_4[Fe(CN)_6]_3$, when ignited gives Ga_2O_3 and Fe_2O_3. It is not precipitated by H_2S in acid solution, but is by NH_4OH in NH_4Cl solution. Many of the gallium-aluminum alloys are liquid and wet glass. The metal itself may be produced by electrolysis of the chloride. The potential of the metal is apparently between indium and zinc, but it is distinctly more difficult than zinc to precipitate. It is one of the few elements that expand on solidifying (like bismuth). Its density near the melting

[1] A critical study of the separation of gadolinium from other metals of the terbium- and ytterbium-earth groups is given in *Z. anorg. allgem. Chem.*, Vol. 109, pp. 1–30, 1919.

[2] Good general references on gadolinium are *Compt. rend.*, Vol. 149, p. 127; and *Chem. News*, Vol. 100, p. 73.

point is variously given at 5.885 to 5.904 as a solid and 6.081 to 6.095 as a liquid. The cubical coefficient of expansion of the liquid is about 0.000055 per degree centigrade, but the metal cannot be used in thermometers, as it wets glass. Its atomic weight is 69.72.

Probably the easiest method of separation of gallium from indium and zinc is by fractional crystallization of the cesium alums.

The metal cannot be separated by electrolysis of sodium hydroxide solutions in the presence of nitrates.

Germanium.—Atomic weight, 72.6. The metal can be detected by a modified Marsh test, using KOH and Al. GeH_4 is formed, which decomposes at 340 to 360°C. The metal is prepared from germanium-bearing zinc oxides (containing also lead, arsenic, cadmium, indium, tin, and antimony) by treating the oxide with hydrochloric acid and then distilling in a slow current of chlorine gas, driving over $GeCl_4$ and $AsCl_3$. H_2S is then passed into the distillate until precipitation is complete. Germanium does not precipitate with H_2S in the presence of ammonium oxalate. The precipitate is dissolved in hot 50 per cent NaOH and Cl_2 passed in to oxidize the arsenic. Add concentrated HCl and continue the Cl_2, and distill. $GeCl_4$ now comes over between 90 and 100°C. free from arsenic. Collect the $GeCl_4$ in water, as hydrated GeO_2. The spectroscope shows traces of sodium, calcium, and iron, which can be removed by redistillation. If the mixed sulphides are roasted at not over 500°C., most of the arsenic can be removed before distillation, without loss of germanium.

At 600°C., 30 per cent of GeO_2 is lost, at 800 to 900°C., 80 to 90 per cent is lost.[1] Samarskite, often given as containing germanium, appears to contain none. Germanium can also be separated from arsenic as the double fluoride (H_2GeF_6), which is not affected by H_2S, whereas arsenic is precipitated in HF solution by H_2S.[2]

Urbain describes the preparation from blende as follows: Dissolve the powdered mineral in concentrated H_2SO_4, and evaporate to dryness. Dissolve in water and add Na_2S. Treat the residue with 15 per cent H_2SO_4, leaching out the ZnS. Treat the insoluble with HNO_3 and evaporate to dryness. Redissolve in H_2SO_4 and from strong acid solution precipitate with H_2S. The precipitate is GeS_2 with a little As and Mo. Add an excess of NH_4OH, neutralize, and throw out the As and Mo, then precipitate from a strong acid solution.

Glucinum.—See Beryllium.

Hafnium is of interest in that Bohr predicted the discovery of this element by his theory of the structure of the atom and it was later discovered by X-ray observations by Coster and Hevesy of Copenhagen. Its atomic number is 72. It resembles titanium and zirconium, and it appears to be found only in company with the latter. Dr. Alexander Scott of London claims to have isolated it as a cinnamon-brown oxide from a New Zealand black-sand deposit. Its atomic weight is 178.6. It is probably present in the black-sand deposit just below Pablo Beach, Fla.

Helvetium.—Proposed as the name for element 85 by Dr. Walther Minder.

Hibernium is a radio element that is assumed to be the origin of the particles that form the rings between the halves of ytterbium mica. It is probably identical with ytterbium itself.

Holmium.—This metal is very like dysprosium, but is element 77; Dy is 76. It is chiefly found in euxenite. It closely resembles didymium, terbium, yttrium, and erbium. The addition of an excess of samarium salt followed by fractional crystallization removes yttrium, europium, and gadolinium. The samarium can then itself be removed as double sulphate (see page 681). Fractional hydrolysis of the phthalates increases the holmium content of a holmium-yttrium mixture, as does also fractional

[1] *Jour. Am. Chem. Soc.*, Vol. 43, pp. 2131–2143, 1921.

[2] *Ibid.*, pp. 2549–2552.

precipitation with sodium nitrite, but dysprosium cannot be so separated.[1] Ethyl sulphate crystallization using alcohol as the solvent is also used.

Illinium.—Element 61 discovered in 1925 by B. S. Hopkins, J. A. Harris, and L. F. Yntema. Named for the state of Illinois.

Indium.—This is one of the rarest of all the elements. It was discovered by Reich and Richter in 1863, and named by them for the two indigo-blue lines that are characteristic of its spark spectrum. It is found mainly in flue dust from zinc smelteries and in metallic zinc.

If metallic zinc is used as the source, the zinc is dissolved in hydrochloric acid, the indium remaining with the lead, undissolved. Indium is precipitated as sulphide in neutral or only faintly acid solution. After freeing from the copper-group metals, the iron and indium may be precipitated together by ammonia, the precipitate redissolved in hydrochloric acid, and the nearly neutral solution boiled with an excess of $NaHSO_3$.

Indium precipitates as a basic sulphite. Metallic indium may be prepared by heating the oxide with hydrogen, by electrolysis of chloride or sulphate solution in the presence of pyridine or hydroxylamine. Metallic aluminum precipitates metallic indium from its solutions at 70 to 80°C. It is a white metal, softer then lead, ductile, and malleable.

It is very like gallium, and fractional crystallization of the double cesium alums is the only effective way of separating gallium and indium. It is stable at ordinary temperatures, but bursts into blue flame on heating.

Lanthanum comes down with the double sulphates (page 681) and is among the more insoluble of the double-magnesium nitrates. It is said that it can be rapidly separated from praseodymium and neodymium by adding a mixture of $4N$ NH_3 and $4N$ NH_4Cl, a drop at a time, at 50°C., using mechanical stirring, but this is a laboratory rather than a commercial method. Fractional precipitation with ammonia in the presence of zinc and ammonium nitrates is also recommended. Specific gravity, 6.17. Lanthanum can be largely separated from neodymium by treating a mixture of their bromides with ethyl benzoate. The Nd reacts much faster to produce the insoluble benzoate, and the first precipitation can be made to consist of 95 per cent Nd benzoate to 5 per cent La benzoate.

Lutecium.—In 1907, when G. Urbain was examining supposedly pure ytterbium nitrate fractions, he obtained different spectroscopic lines for the various portions. He decided that ytterbium was, therefore, composed of lutecium (Lu = 174.99) and ytterbium, 173.4. The reactions are essentially the same for neoytterbium and lutecium. Apparently lutecium is Welsbach's casseiopeium. It is named from the ancient Roman name for Paris, Lutetia.

Masurium is formed by bombarding Mo with deuterons. It is soluble in dilute ammonia and can be separated from most of the Mo in that way. Oxyquinoline precipitates Mo and does not precipitate Ma (*Chem. Abstr.*, Vol. 32, p. 8856[2]).

Molybdenum.—The methods ordinarily given for the treatment of wulfenite (the most common mineral) are to leach with Na_2S, the molybdenum going into solution as Na_2MoO_4, or to fuse with soda ash, sodium hydroxide, and powdered coal, obtaining a lead bullion and a slag from which sodium molybdate may be leached. In either case, the molybdenum is recovered from this solution by precipitation as $CaMoO_4$.

For ferromolybdenum production, the finely ground pulp is mixed with soda-ash solution and heated to boiling, and the molybdenum thrown from the filtered solution by $Fe_2(SO_4)_3$ or $FeCl_3$ and the precipitate smelted with carbon in an electric furnace.

[1] *Cf. Chem. Abstr.*, p. 2072, of 1918.

Molybdenum sulphide is said to be acted on at above 268°C. by chlorine, and it is suggested that pure sulphides could be treated with chlorine and $MoCl_4$ condensed.

Molybdenum has a density of 10.2; tensile strength, 260,000 lb. per sq. in.; melting point, 2550°C.; boiling point, 3617°C.; specific heat, 0.072 cal. per degree centigrade; linear coefficient of expansion, 5.15×10^{-6}; thermal conductivity, 0.346 cal. per deg. per cc.; electrical resistance, microhms per cubic centimeter at 15°C., annealed, 4.8 (all according to Balke). See also page 632.

Nebulium is a hypothetical element[1] not known terrestrially. It is probably a mixture of highly ionized N, O, and S.

Neodymium.—This is found chiefly in cerite, which may be dissolved in acids, and the earths precipitated as oxalates, which are converted into oxides on ignition. These oxides are then treated with nitric acid, which on heating produces basic ceric salts. Lanthanum, praseodymium, neodymium, samarium, and ytterbium are in solution. Crystallization of the nitrates from nitric acid tends to concentrate lanthanum, cerium, neodymium, and praseodymium in the mother liquors. Crystallization of the double-magnesium nitrates tends to throw lanthanum and neodymium into the crystals.

Neothulium.—See Aldebaranium.

Neoytterbium.—In 1908, Urbain announced that he had fractionated ytterbium compounds by a long series of crystallizations into two distinct compounds, the base of one with an atomic weight of 170 (neoytterbium) and the other with an atomic weight of 174 (lutecium). The name neoytterbium has been dropped and that of ytterbium given to this fraction, the unseparated earth often being spoken of as "the old ytterbium." The above weights have since been corrected. See Lutecium, *supra*.

Niobium.—See Columbium, which is the proper name.

Praseodymium comes out in the insoluble double alkali sulphate fraction and then among the less soluble double-magnesium nitrates (see scheme, page 681). Its name means "the green twin." It can be prepared by electrolysis of the anhydrous chloride, which can also be reduced by sodium at 200°C. It is a silvery white, easily tarnished metal, of specific gravity 6.75, which melts at 940°C. and kindles in air at 290°C.

Rhenium accumulates in the Mo-rich material from working up the Mansfeld copper schists for Cu, Co, Mo, and Ni. It is oxidized in sulphate solution with $KClO_3$ to potassium perrhenate and purified by fractional crystallization. Reduction with hydrogen gives the metal. It can also be separated by saturating an alkaline solution containing Mo and Re with H_2S, and refrigerating to −5°C., when rhenium sulphide precipitates, and Mo remains in solution. Voight says metallic rhenium is obtained by electrolyzing alkaline aqueous solutions (D.R.P. 723,303).

Rubidium was discovered in 1861 by Bunsen and Kirchhoff, and named for two dark red lines. It may be recovered from lepidolite by decomposition with sulphuric and hydrofluoric acid; or from any silicate by decomposing with $CaCl_2$ and NH_4Cl and heat. From the first, cesium-rubidium alum can be recovered. From the second, after precipitation of $CaSO_4$ with H_2SO_4, and $CaCO_3$ with $(NH_4)_2CO_3$, the addition of platinic chloride throws down cesium-rubidium chlorplatinate. (See p. 85 also.)

Rubidium metal may be prepared by electrolysis of the fused chloride. It is a soft silvery metal. It melts at 38.0°C. and boils at 696°C. It takes fire spontaneously in air and decomposes water vigorously. It can also be prepared by heating the chloride *in vacuo* with CaC_2 at 700 to 900°C. The metal distills off.

Cesium and rubidium are themselves separated by fractional crystallizations of cesium-iron and rubidium-iron alums, followed by removal of the iron.

Samarium.—Material containing samarium is purified as follows:[2] Cerium is

[1] Nicholson, *Roy. Astron. Soc. M. N.*, Vol. 78, p. 349.
[2] Owens, Balke, and Kremers, *Jour. Am. Chem. Soc.*, Vol. 42, p. 515, 1920.

thrown out by bromine and marble; La, Pr, and Nd by fractionation of the double magnesium nitrates; Eu and Gd by fractionation of the magnesium double nitrates along with the double nitrate of Bi and Mg; and finally the Sm is alternately precipitated as $Sm(OH)_3$ and $Sm_2(C_2O_4)_3$ and recrystallized as hydrated chloride. The bismuth-magnesium nitrate is added and has a solubility intermediate to samarium and europium, so that it thus affords a separation. The last of the bismuth can itself be removed by H_2S. The metal is supposed to melt about 1300°C. It is named for samarskite, in which mineral it was first discovered. Specific gravity is 6.93.

Scandium.—Scandium is chiefly found in the wolframite of Zinnwald, although Nilson discovered it in 1879 in euxenite.

Scandium can be separated from wolframite residues by dissolving the oxides in hydrochloric acid and precipitating with ammonium fluoride.[1] To separate pure scandium salt from this precipitate, lead, copper, etc., are precipitated with hydrogen sulphide from acid solution of scandium chloride; iron and manganese from solutions of scandium-potassium carbonate, the former with potassium-hydrogen sulphide, the latter with iodine in potassium iodide solution; molybdenum is removed as sulphide by precipitation in the presence of formic acid; and the thorium, yttrium, and ytterbium by precipitation of scandium-sodium carbonate, combined with the fractional crystallization of sodium formate.

The scandium is then thrown out of its solutions by HF or H_2SiF_6 or Na_2SiF_6 in acid solution, after which it will contain only small amounts of thoria, yttria, and ytterbia. It can be further purified by precipitation with $Na_2S_2O_3$, but will probably still contain about 1 per cent of thoria.

The $(NH_4)_3ScF_6$, precipitated by addition of ammonium fluoride to scandium salts, also can be used for fractionating. This salt hydrolyzes to $(NH_4)_2ScF_5$ and NH_4ScF_4.

Pure scandium is diamagnetic. Yttrium and celtium are the closest related elements. The atomic weight is now ordinarily given as 45.1.

M. Speter says scandium can be separated directly by decomposing its minerals by acid, or fusing them with alkali and dissolving the melt in acid. The acid solution is filtered, the rare earths precipitated as oxalates and boiled with H_3PO_2, filtered again, the precipitate taken up in sulphuric acid and reprecipitated as oxalate.[2]

Scandium is one of the three elements clearly forecast by Mendeléef. His "ekaluminum" is gallium, "ekasilicum" is germanium, and "ekaboron" is scandium.

Selenium.—This element was discovered in the dust collected in acid-chamber flues by Berzelius in 1817. It is widely distributed in the ores of lead, copper, gold, and silver and in pyrites. The chief source of the commercial metal is the flue dust from plants treating electrolytic copper slimes. There are a number of allotropic forms. From the metallurgical standpoint only three varieties are important: the finely divided material produced by precipitating selenium from chloride solutions with sulphur dioxide or carbon monoxide (the former being the common commercial precipitant); vitreous selenium; and metallic selenium. If the first form, which is a bright-red to dark-brown precipitate (this precipitated modification itself runs through several allotropic forms), is heated it melts to a black mass, which, when cooled quickly, gives a black to purple-black vitreous bar when viewed by reflected light and a beautiful red if drawn while hot into thin sheets. When the vitreous modification is kept for some time at a temperature of 150°F. or over, it changes to a silvery-gray modification (metallic selenium), which is unique among metals in having its electric conductivity greatly altered by changes in the intensity of the light with which it is illuminated.

[1] STERBA, J., *Z. Elektrochem.*, p. 289, 1914.
[2] German patent 282657, 1941.

The resistance falls with increased illumination and increases as the temperature increases.

The change from the vitreous to the metallic state is strongly exothermic and becomes more rapid as the temperature increases up to about 125°C. The metal melts at 217°C.

The metallic modification can be changed back to the vitreous by melting and quick cooling.

The refining of selenium and tellurium has become "big business." Two of the modern plants have allowed their recovery methods to appear in the Institute of Metals Division volume of the American Institute of Mining and Metallurgical Engineers for 1943, both being reprinted from *Metals Technology* of 1938. Frederic Benard describes the plant of the Ontario Refining Co. at Copper Cliff, and C. W. Clark and J. H. Schloen describe that of the Montreal East plant of Canadian Copper Refineries Ltd. The following is based on their articles.

Modern selenium recovery by copper refiners is largely based on a slow roasting of the copper slimes with sulphuric acid. The dried slimes are mixed with 75 per cent of their weight of 60 per cent Bé. sulphuric acid. Additional acid is also added in the form of a spray on two of the roasting hearths during the roasting operation, at the Montreal East plant. Roasting is carried on at 700 to 800°F.; the combustion gases from the roasting furnaces being sent through the silver-refining scrubber system to avoid any possibility of loss of metal, while the roasting gases, which contain about 85 per cent of the selenium, are handled through a separate scrubber and Cottrell fume-recovery system. The scrubber solution is treated for selenium whenever the selenium content builds up to 1 lb. per cu. ft. of solution.

The roasted slimes are leached with water, which eliminates most of the copper They are then treated with 10 per cent caustic soda solution which removes about 85 per cent of the tellurium. The solution from this soda leaching is later used to leach the soda slags from the doré furnaces. In smelting the slimes, the first slag is taken off, which contains chiefly lead, arsenic, antimony, and iron, and the residue left in the furnace is treated with fused soda ash and blown with air, most of the selenium and tellurium being converted to sodium selenite and tellurite. The residue can also be treated with scrap iron, which breaks down the selenium matte and renders the blowing unnecessary. In either case, the soda slag is leached with the caustic solution from the previous slime treatment.

The caustic soda leach is neutralized with sulphuric acid, which precipitates the tellurium dioxide, the selenium remaining in solution.

This neutralized solution and the scrubber solutions are acidified with 10 per cent of their weight of 66°Bé. sulphuric acid and are treated with sulphur dioxide. Precipitation is carried on between 60 and 90°F.; below 60° too large a quantity of sulphur dioxide gas is required to saturate the solution, while above 100° the selenium becomes plastic and is difficult to clean out from the precipitator and always occludes a certain amount of sulphuric acid. Selenium cannot be precipitated completely from straight sulphuric acid solution so that the solution after precipitation will still carry about 0.5 g. per l. Se and about 0.2 g. per l. Te.

The selenium precipitate is washed and added to the crude selenium from the scrubbers and Cottrell installations, and this selenium is distilled using cast-iron retorts at just above the distilling point of selenium. This gives a selenium product containing less than 0.1 per cent Te. The retort residue is ground and sent back to be roasted with the raw slimes. The precipitate from neutralization of the caustic soda leaches carries about 32 per cent Te, 6.5 per cent Se, and 2 per cent Cu. This mud is mixed with sulphuric acid and roasted for about 8 hr., which eliminates most of the selenium as a fume and converts the copper to water-soluble sulphate.

Tellurium cannot be precipitated from a straight sulphuric acid solution, so about 2 per cent of salt is added before passing in sulphur dioxide. The tellurium precipitates and is filtered, washed, and melted, the bars containing about 99.7 Te, 0.07 Se, and 0.03 Cu.

For the recovery of selenium from acid-chamber residue and similar material of the sort, the process originally introduced by the author of leaching these residues with sodium chlorate and hydrochloric acid can be used. After filtering these solutions, the selenium is precipitated by sulphur dioxide. If tellurium is present, it is not precipitated by sulphur dioxide if the strength of the hydrochloric acid is up to 50 per cent. If tellurium is present, it can be recovered after the selenium has been filtered off by diluting the solution and allowing it to stand.

The selenium precipitate is washed and dried, then either powdered, or melted in enamelware pans and cast.

The leaching operation is most conveniently carried on in stoneware tanks, the precipitation either in stoneware jars, or, even better, in barrels painted with P. & B. paint. The precipitation should not be carried on too fast or the precipitate will occlude sulphuric acid, which oxidizes the metal during drying and melting; nor should the precipitation be from too concentrated a solution or a purplish-black modification will result which is very hard to dry and very difficult to melt.

The compounds of selenium are analogous to those of sulphur. The hydride, H_2Se, is worse-smelling than the sulphur compound and more poisonous. A bubble of the pure gas is said to have paralyzed for 6 months the olfactory nerves of its discoverer. It forms SeF_2 (soluble in HF, hydrolyzed by H_2O); Se_2Cl_2, $SeCl_4$, Se_2Br_2, $SeBr_4$, Se_2I_2, SeI_4, and various complex chlorbromides and oxyhalides. It forms SeO_2 and SeO_3, which are the anhydrides of corresponding acids. Selenic acid is unaffected by SO_2 or H_2S (differs from selenious acid in these particulars), but is slowly reduced by boiling concentrated hydrochloric acid. Barium selenate is completely decomposed by hydrochloric acid, as is also the tellurate, thereby differing from barium sulphate.

Reactions of importance from the metallurgical standpoint, in addition to those given above, are: The amorphous-powder modifications are soluble in potassium cyanide, forming KCNSe. Tellurium is insoluble (this gives a method of separation). Those amorphous modifications precipitated at low temperatures are soluble in carbon disulphide, but those precipitated at or heated to high temperatures are not soluble, nor is tellurium. Both selenium and tellurium go into colloidal dispersion when heated with strong sulphuric acid, the beautiful purple produced by tellurium being a characteristic test for it. The metals again precipitate on cooling or dilution. If, however, the heating is carried on long enough, the metal is oxidized, forms sulphates, and is no longer reprecipitated on cooling or dilution.

Both selenium and tellurium and their compounds when heated with an alkaline carbonate and carbon form alkaline selenides and tellurides which are decomposed by the passage of air through their solutions. This is the process introduced by A. E. Knorr for the recovery of tellurium from high-tellurium flue dusts.

$$Na_2CO_3 + Te + 2C = Na_2Te + 3CO$$
$$2Na_2Te + O_2 + 2H_2O = 2Te + 4NaOH$$

Metallic selenium has a specific gravity of 4.8 and melts at 217°C. The specific gravity of the vitreous modification is 4.28 and of the amorphous about 4.26. A red crystalline modification has a specific gravity of 4.47 and seems to melt between 170 and 180°C., but passes over quickly to the metallic modification and solidifies, giving out 55 cal. per g. Selenium boils at 680°C. at 760 mm., at about 310°C. at low pres-

sures. It burns in air with a blue flame, forming SeO_2, but the reaction requires external heat to maintain it. Above 250°C. it unites with hydrogen, more quickly as the temperature is raised.

The chief use of selenium in tonnage is as a coloring matter for ruby glass. It is also used in electrical devices such as automatic light controls, etc., where its varying conductivity under varying illumination is of use, but the weight used in a selenium cell is almost negligible.[1]

Tantalum.—The metal is usually prepared from tantalite, the most important of the tantalum minerals. The finally pulverized tantalite is fused with potassium hydroxide, converting the tantalum and columbium to soluble tantalate and columbate. The melt is then dissolved in water, and after filtration the solution is neutralized with hydrofluoric acid, converting the columbate and tantalate into double fluorides with potassium. (If sodium hydroxide is used, the sodium tantalate and columbate that are formed are not soluble.) After neutralization with hydrofluoric acid, the potassium-tantalum fluoride, K_2TaF_7, precipitates and can be purified to any desirable extent by recrystallization. The columbium forms a potassium-columbium oxyfluoride, $K_2CbOF_5.H_2O$, which is fairly soluble in water and in dilute hydrofluoric acid.

Tantalum pentoxide can be formed by treating the potassium-tantalum fluoride with twice its weight of concentrated sulphuric acid at about 350°F. for 2 to 3 hr. to drive off all the hydrofluoric acid. The resulting solution is amber colored, and when this is poured slowly into boiling water it is hydrolyzed and dense white insoluble tantalic acid is formed. The precipitate should be washed with hot dilute sulphuric acid, then with water, and filtered. If this precipitate is dried at 120°C. for several hours, it can be powdered readily. Ignition of the powder at 1000°C. yields Ta_2O_5. This oxide is reduced *in vacuo*, which produces the metal.

An alternative method based on the insolubility of sodium tantalate is based on the fusion of tantalite with sodium hydroxide. The addition of a little sodium carbonate to the melt lowers the melting point greatly. The concentrate should be ground to about 100 mesh and added a little at a time to the fused alkali. R. H. Myers and Dr. J. Neill Greenwood, of the University of Melbourne, state that the optimum mixture is ground ore 1 part, caustic soda 2.7 parts, and sodium carbonate 0.3 parts.[2] The mixture can be melted in iron crucibles, and iron rods used to stir it. A final fused temperature of about 800°C. must be reached.

The melt is poured on a clean iron or steel plate and allowed to cool in a thin layer and broken up while still hot. It is then heated with hot water, and after the lumps have completely disintegrated, the suspension is set aside to cool to room temperature. The strong alkaline supernatant solution attacks filtering media, so it should be decanted from the insoluble matter, which is then washed with cold water. The insoluble residue is mainly sodium tantalate and sodium columbate together with iron and manganese compounds. The method has the advantage on low-grade ores of removing most of the silica, most of the tin, and practically all the aluminum as silicate, stannate, and aluminate, together with some of the titanium, as titanate.

The insoluble residue is then heated to boiling in suspension in hot water, and sufficient concentrated hydrochloric acid added to decompose the sodium salts, giving insoluble columbium and tantalum pentoxide, with sodium, iron, and manganese chlorides in solution. These oxides are separated by solution in hydrofluoric acid and are then fractionally separated as indicated earlier in this section.

[1] For laboratory tests for impurities in selenium and for select methods of selenium assay, reference should be made to LENHER, VICTOR, Occurrence, Chemistry and Uses of Selenium and Tellurium, *Trans. A.I.M.E.*, New York meeting, February, 1923.

[2] *Proc. Australasian Inst. Mining Met.*, No. 129, new series, March, 1943, p. 43.

According to French patent 834104, columbium and tantalum can be reduced by calcium carbide. Selective reduction is possible by using an insufficient amount of carbide to precipitate both metals. The columbium is reduced first.

Columbium pentoxide can be reduced with carbon at atmospheric pressure at temperatures above 1660°C. The metal can also be prepared by mixing columbium oxide and columbium carbide in stoichiometric proportions as powders and pressing the mix, then heating it at a temperature below but close to the volatilizing point of the oxide. After the reaction is complete, the temperature can be raised and a fused metal results.[1]

Tantalum is not attacked by aqua regia or nitric or hydrochloric acid, either hot or cold. Solutions of caustic alkalies do not attack it. It is slowly attacked by boiling concentrated sulphuric acid and by hydrofluoric acid. It is rapidly attacked by a mixture of nitric and hydrofluoric acids. When tantalum is heated in air, the surface becomes blue at about 400°C., and at a somewhat higher temperature nearly black. Above a dull-red heat the white oxide is produced and the metal gradually burns. The metal combines readily at elevated temperatures with hydrogen, nitrogen, and chlorine (the last producing the volatile pentachloride). The metal is tough and highly ductile and malleable.

As an electrode the metal is of interest. Gold or platinum may be deposited on tantalum and removed with aqua regia. If two plates of bright tantalum are immersed in an electrolyte and a direct current passed, film forms on one plate in a few seconds and the voltage drops. With sulphuric acid of the strength ordinarily used for electric storage batteries, the current is less than 1 milliamp. with a voltage up to 75.

If a tantalum and a lead plate are placed in an electrolyte and an alternating current passed, the current in one direction is shut off and a pulsating direct current obtained. Hydrogen gas is given off at the tantalum plate.

Tantalum has a density of 16.6; atomic volume of 10.9; tensile strength, small wires, 130,000 lb. per sq. in.; compressibility per kilogram per square centimeter, 0.50×10^{-6}; Young's modulus of elasticity, 19,000 kg. per sq. mm ; melting point, 2850°C. (?); specific heat, 0.0365; linear coefficient of expansion per degree centigrade, 7.9×10^{-6}; thermal conductivity, calories per cubic centimeter per degree centigrade, 1.30; electrical resistance (annealed), microhms per cubic centimeter at 15°C., 14.6; electrical coefficient of resistance, 0.00335 per degree centigrade. Discovered in 1802 by Eckeberg; named for Tantalus.

Tellurium.—The presence of this element was suspected by Müller von Reichenstein in 1782 in a sample of gold ore from Austria, and was isolated in 1798 by Klaproth. It is of common occurrence as sylvanite (gold telluride), particularly in Colorado.

The metallurgy is intimately connected with that of selenium and reference should be made to what has been said on that metal (pages 692 to 693).

Tellurium is a silver-white metal, atomic weight, 127.5; melting point, 452°C.; boiling point, 1390°C. (760-mm. pressure); density, 6.2; tensile strength, 115 kg. per sq. cm.

It is used as a crystal detector in radio work, as a coloring matter in glass and ceramic trades, and, in the form of diethyl telluride, is an antiknock compound in the internal-combustion engine, and is a valuable reagent for the removal of cobalt from electrolytes in the Tainton process.[2]

It unites readily with chlorine, forming $TeCl_2$ and $TeCl_4$, and with oxygen, forming TeO_2 and TeO_3, which form acids H_2TeO_3 and H_2TeO_4, analogous to sulphurous and

[1] BALKE, C. W., *Ind. Eng. Chem.*, June, 1923, p. 560.

[2] *Minerals Yearbook*, 1938, p. 683.

sulphuric, except that tellurous acid is more stable and telluric acid less so than the sulphur analogues.

It is a brittle crystalline-structured metal, tarnishing slowly in air, but less so than lead. Its compound with hydrogen, H_2Te, has a frightful odor. It is peculiar in that it is eliminated almost entirely from the body as methyl telluride, via the lungs, giving a garlic odor to the breath.

Tellurium combines readily with many metals when heated. The telluride of aluminum can be formed by dropping tellurium into molten aluminum. This telluride is an interesting substance, decomposing with water to give aluminum hydroxide and hydrogen telluride, which is highly poisonous and almost intolerably offensive.

Magnesium telluride is similarly formed, with explosive violence. In general, in making selenides and tellurides by addition, a mask and goggles should be worn.

Terbium, found chiefly in gadolinite, belongs to the Sm-Nd-Gd-Pr group. The main difficulty is to free it from holmium and dysprosium. Its bromate is more soluble than theirs, its nitrate and chloride less so. Its name is derived from Ytterby, near which town gadolinite was first found. Terbium oxide is black.[1] Crookes' original element "ionium," not the radium decomposition product, seems to have been terbium.

Another separation is by the crystallization of the dimethyl phosphate.[2] See under Dysprosium. It is also said that terbium can be oxidized by $KClO_3$ to TbO_2 and can thus be separated from all other earths but Pr.[3]

Thallium is chiefly found in acid-plant flue dust, its extraction depending on the solubility of the sulphate and sparing solubility of the chloride. It is also found in the residues from the purification of Cd. The flue dust is boiled with dilute H_2SO_4 in wood or earthenware containers, filtered, and HCl added. The precipitate is dissolved in H_2SO_4 and thallium again thrown down. Salt can be used instead of HCl. The metal can be obtained by fusing the chloride cautiously with KCN and Na_2CO_3, or it can be reduced by zinc and melted in an inert gas, but A. Kolliker[4] says the metal on washing quickly oxidizes and then dissolves, affording an easy separation from other metals. The metal is highly toxic, probably ranking next to mercury among the elements. The metal melts about 301°C. While most authorities say that Tl_2O_3 dissolves readily in HCl, this seems very doubtful.

Thallium is one of the few metals whose lower oxide is more stable than the upper. Its binary alloys with lead have a decidedly higher melting point than has either constituent, indicating possibilities in their use as insoluble anodes[5] and for acid-chamber linings. Lead-thallium and lead-thallium-tin alloys also have theoretical possibilities as high-temperature solders.

Thorium.—Atomic weight, 232.15; melting point about 1800°C. The principal commercial mineral carrying thorium is monazite, although small quantities of thorianite and thorite have been used commercially. These latter minerals, however, are limited in quantity. Monazite is composed mainly of phosphates of the cerium and lanthanum earths together with a variable percentage of thoria. Its specific gravity is 4.8 to 5.5, and its color varies from yellow-gold to reddish brown and is occasionally even dark brown or black. Monazite occurs in certain gneissic and granitic rocks, but the actual commercial deposits which are worked are alluvial. The principal sources are Brazil and India, although the mineral has been mined success-

[1] For a general resumé of the work on terbium see articles by URBAIN, G., *Chem. News*, Vol. 100, p. 73; *Chem. Ztg.*, Vol. 33, p. 745.

[2] PRANDTL, *Zeit. anorg. allgem. Chem.*, Vol. 238, p. 225, 1938.

[3] *Angew. Chem.*, Vol. 52, pp. 536–537. Its valences are said to be 3 and 4.

[4] *Chem. Ztg.*, Vol. 43, p. 231.

[5] An alloy experimented with by Dr. Colin G. Fink and highly resistant in acid sulphate solutions containing both HNO_3 and HCl was: Pb, 70; Sn, 20; Tl, 10 per cent.

fully in the United States, in the Carolinas, Idaho, and Florida. It has been found in Switzerland, Africa, and Australia, and to a limited extent in river rocks and placers in Ekaterinburg, Russia.

Monazite is usually found in gravels of small streams and in bottom lands. In Brazil and India it occurs mainly in the beach sands of sea water. It is found in small crystals in gneiss, granite, and pegmatite rocks. As these rocks become disintegrated the crystals are washed into the creeks and streams and, together with other heavy sands, are deposited in the beds of watercourses. On the coast of Brazil the monazite from the crystalline rocks of the coast mountains is concentrated in the sea sands by the waves of the sea. The bulk of the monazite in Brazil is found in the states of Espirito Santo and Bahia. In India, the main location is in the Travancore district in southern India. The deposits of the Carolinas in the United States cover an area of several hundred square miles east of the Blue Ridge Mountains. Practically all the monazite mined in the Carolinas is derived from the gravel in the streams and bottom lands, the miners usually following the course of the streams and creeks. The gravels vary greatly in thickness; in general, they are between 1½ and 2½ ft. thick. Monazite is also found in Florida.

Extraction from the Ores.—The methods of treating monazite for the production of thorium nitrate are more or less secret and are changed from time to time, depending upon conditions, costs of chemicals, etc. The general principles of the commoner method used before the First World War are as follows: The mineral is heated in cast-iron pans or pots with about twice its weight of concentrated sulphuric acid, until the monazite is completely decomposed, giving a white mass of sulphates, which are largely insoluble in the acid. This mixture is run into cold water in a lead-lined vat and the whole stirred until solution is complete. The material is allowed to stand for a considerable period in order that the insoluble matter, consisting of silica, zircon, rutile, and other minerals insoluble in concentrated sulphuric acid, may settle out, and the solution that contains the rare earths, phosphates, etc., is decanted off. If now the free acid is partially neutralized so as to reduce the acidity, thorium phosphate is precipitated first, because it is less soluble than the phosphates of the other rare earths. The thorium phosphate still carrying quantities of other rare-earth phosphates is filtered, dissolved in a minimum amount of acid, and the fractional precipitation repeated.

One method of still further purifying the precipitate is to boil it with oxalic acid,[1] which causes the thorium to be precipitated as thorium oxalate, while the phosphoric acid remains in solution. The precipitated oxalates are digested for a prolonged period with sodium hydroxide, and the hydroxides formed are dissolved in hydrochloric acid. If the acid solution is then carefully treated with sodium hydroxide, until about one-sixth of the bases have been precipitated, thorium hydroxide will be precipitated before the other hydroxides. Baskerville has suggested the volatilization of the phosphoric acid by mixing 1 part of monazite with 1.1 parts of petroleum coke, 0.8 parts of lime, and 0.15 parts of fluor spar, and heating in an electric furnace. This not only removes the phosphorus, but also gives the latter in a marketable form. Further purification of the thorium hydroxide may be carried on in one of several ways. The oxalate method depends upon the fact that thorium oxalate forms a double salt with ammonium oxalate, which is soluble, while cerium oxalate is almost insoluble. The carbonate method is based upon the fact that thorium carbonate forms double salts with the alkali carbonates, which are soluble, whereas the double salts of the cerium earth oxalates are insoluble. The sulphate method depends upon the fact that certain hydrated sulphates of thorium possess a considerable difference in solubility from the sulphates of the cerium earths. This fact is used as a basis for fractional crystallization. Whichever method is used, after the thorium is sufficiently purified it is con-

[1] *Jour. Phys. Chem.*, Vol. 20, p. 640, 1916.

verted into thorium carbonate or hydroxide and dissolved in nitric acid and the solution evaporated until thorium nitrate, $Th(NO_3)_4.4H_2O$, crystallizes out. After the beginning of the First World War, owing to the greatly increased cost of certain chemicals, especially oxalic acid, considerable modifications were necessary in the process used for treating monazite sand. These changes in practice have been kept secret, but consist essentially in combinations of the methods described above.

In a British patent[1] the following method is described. The crude thorium phosphate is boiled with caustic and then dissolved in sulphuric acid. Thorium fluoride is precipitated by hydrofluoric acid and dissolved in sodium bicarbonate. Thorium hydrate is precipitated by caustic soda, converted to sulphate, and crystallized. The sulphate crystals are converted to hydrate with ammonia and the cycle repeated. The thorium is finally converted to the nitrate.

The element mesothorium, a radioactive product of thorium and hence a constituent of all thorium minerals, deserves mention, since it is now being recovered as a by-product in the refining of monazite.[2] Barium chloride (0.2 per cent of the weight of ore) is added to the ore, and then sulphuric acid. After dilution, the slimes containing the mesothorium and barium sulphate are decanted from the coarse residue, settled or filtered out of the solution, and treated for the further concentration and recovery of the mesothorium.

Concentration Methods.—The first stage of concentration in the Carolinas involves the use of oscillating tables or sluice boxes. The concentrates produced in the sluice boxes contain 20 to 60 per cent monazite. The crude concentrates must be further refined, and are best treated by electromagnetic separators, of which the Wetherill type has proved to be the most successful.[3] The separation of the minerals is dependent on the difference in their magnetic permeability. The magnets are best adjusted so that the first pole of the first magnet removes from the sand the highly magnetic material, as, for instance, the magnetite and ilsemannite; the second pole of the first magnet extracts the garnets and also the finer grains of the ilsemannite; the third magnet (being the first pole of the second magnet) removes all the coarser grains of the monazite; and the last pole extracts the finer grains of the monazite. At the end turn of the rubber belt of the machine, the residues are dropped into a receptacle.[4] The grade of the concentrates obtained from the different large sources of supply varies considerably. The average concentrate obtained in the Carolinas was about 3½ to 4 per cent thorium oxide, whereas that obtained from Brazil averages around 6 per cent. It was for this reason very largely that the industry in the Carolinas was ultimately given up. The monazite from India has even a higher grade than that from Brazil, averaging around 9 per cent thorium oxide, and some of it going still higher. A concentrate of this type carries about 27 per cent cerium oxide, 29 per cent lanthanum and allied oxides, and 2 to 4 per cent yttria and allied oxides. It also contains about 26 per cent phosphoric acid.

Metallic Thorium.—The metal has probably not yet been prepared in a perfectly pure state. Reduction of the oxide with magnesium is never complete, and attempts to reduce with carbon give a mixture of the metal and carbide. Moissan and Honigschmid heated the purified anhydrous chloride with sodium in a sealed glass tube and obtained a product that was said to contain only 3 per cent of the oxide. The amorphous metal is a dark-gray powder of specific gravity 11.3, and when hammered and strongly heated it has a density of 12.16. It burns readily in air, and melts at about 1700°C., although the pure metal would probably melt at a higher temperature.

[1] British patent 179399.
[2] *U. S. Bur. Mines Tech. Paper* 265.
[3] GUNTHER, "Electromagnetic Ore Separation," 1909.
[4] KITHIL, *U. S. Bur. Mines Tech. Paper* 110.

Uses of Thorium.—The main use of thorium is in the incandescent gas-mantle industry. The successful use of incandescent gas mantles began in 1893 when Welsbach patented the use of a mixture containing 98 to 99 per cent thorium oxide with 1 to 2 per cent cerium oxide (English patent 124 of 1893). With this mixture the oxides give a brilliant light and have a maximum illuminating power. The cerium oxide is probably in solid solution in the thorium oxide.[1] Thorium oxide is a very poor heat conductor and hence can be raised to a high temperature. The small amount of cerium oxide gives enough color for efficient light emission. An outline of the methods used for obtaining mantles is as follows: The mantle itself is made either of ramie fiber or of artificial silk. The woven mantles are thoroughly washed in a 2 per cent solution of nitric acid, distilled water, and then in dilute ammonia. The latter is thoroughly washed out by distilled water. The mantle is dried in a current of hot air and then dipped in a solution of thorium and cerium nitrates, consisting of 99 per cent thorium salt and 1 per cent of cerium.

Small quantities of beryllium or magnesium nitrate are added for strengthening purposes. The upright mantles are then fitted with an asbestos loop by which they are suspended, whereas the inverted mantles are fixed to a supporting ring. Those portions on which there is especial strain are sometimes treated with a thorium solution containing much larger proportions of calcium, aluminum, or magnesium salts. The mantle is then shaped and burnt off from the top downward by applying a Bunsen flame. During this process of burning off, there is considerable shrinkage. As soon as the carbonization is finished, the mantle is shaped and heated with low-pressure burners, after which it is hardened by heating in a high-pressure burner. The mantles, now consisting of nothing but the ash skeleton, are immersed in a collodion solution containing collodion, ether, camphor, and castor oil. The ingredients may vary to some extent. After drying at a moderate temperature, the mantles are ready for use.

Thulium.—Thulium was discovered in 1879 by Cleve, when he was attempting to find out what gave the rose color to the salts of "old erbium." He named it for "Thule," an old name for Scandinavia. It is among the most soluble of the double nitrates. (See scheme on page 681 for its separation.) In solution with cerium and yttrium only, it is completely separated from them by precipitation with H_2SiF_6.

Titanium.—The chief commercial source of titanium is ilmenite, from which it is recovered by dissolving in concentrated sulphuric acid and then adding sodium chloride to the concentrated solution to throw down sodium-titanium sulphate.

Alkaline hydroxides or carbonates precipitate titanium hydroxide from solution, a bulky gelatinous precipitate. The metal can be produced from the oxide by the Thermit reaction.

The Carteret-Devaux process for the production of the metal is to reduce ore at red heat with coal, then to heat the reduced mass with chlorine gas at gradually increasing temperatures, distilling off successively iron, silicon, and titanium.

In the preparation of pure titanium from the chloride Maurice Billy recommends sodium hydride for the precipitant.[2] $TiCl_4 + 4NaH = Ti + 4NaCl + 2H_2$. The purified oxide can also be reduced by heating in a current of hydrogen gas. George F. Comstock[3] says that TiO_2 can be successfully reduced by Na and Ca, but not by Al. $TiCl_4$ can be reduced by Mg in an atmosphere of argon.

Billy states that by reducing titanium dioxide with titanium it is possible to obtain the following:

Between 700–800°C., a blue oxide, Ti_3O_5.

Between 900–1000°C., a violet oxide, Ti_2O_3.

[1] WHITE and TRAVERS, *Jour. Soc. Chem. Ind.*, Vol. 21, p. 1012, 1902.
[2] *Ann. chim.*, July-August, 1921.
[3] *Metals & Alloys*, Vol. 9, pp. 286–290, 314–318, 1938.

Between 1100–1200°C., a black oxide, Ti_3O_4.

Between 1400–1500°C., a brown oxide, TiO.

Titanium tetrachloride is an important smoke-screen compound, through its hydrolysis with the water vapor of the air.

Titanium is important as an alloy metal for permanent magnets, using 15 to 30 per cent Ti, 1 to 5 per cent Mn, 0.6 to 1.2 per cent C, with or without 2 to 5 per cent of Cr. Steels containing 10 to 30 per cent Cr, 5 to 12 per cent Ti, and 3 to 5 per cent Mo are said to be highly resistant to corrosion.

Titanium is brittle when cold, but can be forged at red heat. So far it has proved impossible to draw it into wire. It is interesting that in the iron blast furnace titaniferous ores give copper-colored cubes of $Ti(CN)_2.3Ti_3N_2$ in the slag.

Victorium.—A metal reported by Crookes, apparently gadolinium.

Ytterbium.—See Europium, above.

Yttrium.—This metal forms a soluble double-alkali sulphate and is among the more soluble double nitrates (*cf.* pages 681 and 682). Probably the best separation from the other members of the yttrium group (Dy, Ho, Er, Tm, Yb, and Lu) is the classic "fused-nitrate" method (see page 682), but fractional precipitation as the cobalticyanide or as the nitrite [using $K_3Co(CN)_6$ for the precipitant with the first and $NaNO_2$ for second] gives fair separations. The Yt remains in solution. Fractional precipitation with potassium chromate does not remove erbium or holmium; the nitrite does. Yttrium mixed metal can be produced by decomposing the anhydrous chlorides *in vacuo* with sodium or by electrolysis of the mixed chlorides. It is a blue-gray color and disintegrates in time to powder, especially if exposed to moist air. The element derives its name from the Swedish town of Ytterby. Atomic weight, 88.92; melting point, about 1490°C.

Zirconium can be produced by the reduction of $ZrCl_4$ with metallic sodium. It alloys well with Ni, Cu, Au, Al, Mg, and W. The oxide ZrO_2 becomes practically insoluble on strong ignition in every acid except hydrofluoric, and doubtless the conflicting statements as to solubility merely reflect differences in ignition temperatures. The specific gravity of the metal is about 6.4.

Bruère and Chauvenet say there is but one nitride (Zr_3N_4). In reducing atmosphere, the oxide has a strong tendency to form carbides.

It is said that a pure ZrO_2 can be obtained by heating zircon with $1\frac{1}{9}$ times its weight of carbon to whiteness, then treating with dilute sulphuric acid and filtering. $Zr(SO_4)_2$ is in solution.

The acetate is apparently a hydrophilic colloid.[1] It is soluble in water in all proportions, can be salted from its aqueous solutions like soap, and when shaken the solution lathers quite freely. Evaporation of the solution causes no crystallization, but results in an amorphous mass resembling gelatin. Solution of the residue from this evaporation takes place very much after the manner of the solution of gelatin, with first a swelling and softening and then a gradual dissemination of this gel through the liquid. It is in the exploitation of these peculiar properties of the zirconium compounds that the most important industrial applications may yet be found. The hydroxide is a strongly adsorptive compound.

Salts of the metal hydrolyze strongly, and Rodd[2] says no normal salt exists in aqueous solution. Also the extent of the hydrolysis seems to depend on the method by which the salt was prepared.

Zirconium is precipitated from its weakly acid solutions by sodium thiosulphate. The phosphate precipitates in strong mineral acid solutions, but the precipitate is difficult to wash and can be broken up only by fusion with caustic soda.

[1] Nonamaker, *Chem. Met. Eng.*, July 28, 1924.

[2] *Chem. Soc.*, Vol. 111. p. 396, 1917.

For extracting ZrO_2 from the ores, Marden and Rich say that for commercial extraction the best method is to heat 1 part of ore with 4 parts of concentrated sulphuric acid until fumes have ceased and then raise the temperature to 650°C. After cooling, extract with 50 parts of cold water and filter, then add sodium carbonate until $Zr(OH)_4$ just begins to form. Allow the solution to stand 3 or 4 days, during which $4ZrO_2.3SO_3.14H_2O$ will gradually settle out. This is ignited to give ZrO_2.[1]

Another method recommended for the treatment of zirkite is to sift 100-mesh material into a fused mass of 3 parts sodium carbonate and 3 parts sodium hydroxide. Fuse for 1 hr., cool, crush, and leach with hot water. The washed residue is then digested with 1:1 HCl and the solution filtered. Neutralize with soda ash as far as can be done without precipitation, and pass SO_2 into the hot solution.

Zirconium melts about 2800°C., above Mo and close to Ta.[2] The melting point of the oxide is given anywhere from 2560 to over 3000°C. If the metal actually melts at 2800°C., the higher value for the melting point of the oxide would seem correct.

A. J. Phillips[3] says the best way to produce $ZrCl_4$ is to bubble Cl_2 through hot water and then pass the moist gas through a retort heated to about 500°C. and filled with small balls of zirconia and petroleum coke. The following table of chlorination temperatures is given.

CHLORINATION BY MIXTURES OF Cl_2 AND CO

	CO in excess	Cl_2 in excess
ZrO_2	480	425
SnO_2	400	
MgO	475	
Al_2O_3	450	
Fe_2O_3	460	370
Cr_2O_3	625	
MnO_2	460	
U_3O_8	500	

Treatment of Platinum Concentrates.—In general, the recovery of the platinum-group metals is based on their solution in aqua regia and their recovery as double-ammonium chlorides.

In the treatment of crude platinum concentrates, the first step is a 24-hr. leaching with 3 l. of 20°Bé. hydrochloric acid and 1 l. of 35°Bé. nitric acid per kilogram of platiniferous material, keeping the mass (held in porcelain vessels) at 80°C. The insoluble residues from several portions thus treated will ordinarily be combined and treated again in the same manner for the recovery of further platinum. The insoluble residue from this re-treatment is eventually treated for the recovery of iridium and osmium (see pages 702–703).

The solution is decanted from the insoluble residue and evaporated with the addition of about 1 l. of hydrochloric acid to each 6 or 7 l. of first solution. The evaporation should be carried to 140 or 150°C., in order to alter the iridium to such a form that it will not precipitate with the platinum in the next step.

Redissolve the evaporated mass in hot water, and allow to stand for a few hours.

[1] *Jour. Ind. Eng. Chem.*, Vol. 12, p. 651.
[2] COOPER, HUGH S., *Jour. Am. Electrochem. Soc.*, 1923, p. 222.
[3] *Jour. Am. Ceram. Soc.*

Usually a residue of gold and platinum will separate out. This residue should be calcined, redissolved in aqua regia, and the gold thrown down with $HNaSO_3$ after evaporation with additional hydrochloric acid. Ferrous sulphate can also be used. The filtrate from the gold is added to the original platinum solution.

The platinum solution is then brought to 30°Bé. (ordinarily it will be stronger than that), and a 30 per cent ammonium chloride solution added, 2 l. of ammonium chloride solution per liter of platinum solution, pouring it in gradually with energetic stirring.

Allow to stand about 3 or 4 hr., not longer, or iridium will begin to separate, and then filter off the precipitate and wash with 20 per cent ammonium chloride solution, about 1 l. of wash solution being used for each 2 l. of original platinum solution. The precipitate should be canary yellow.[1]

The precipitate is dried in crucibles and is then calcined about 8 hr. at between 700 and 800°C., the heat being raised gradually. Fused silica ware is best for this, as even 1 per cent of iron in a clay crucible contaminates the material with iron. The atmosphere should be strongly reducing.

The product of this calcination is known as "platinum moss." It is crushed in a mortar and boiled in 1:5 hydrochloric acid to remove any adhering iron.

If the moss is to be used to produce an agglomerated mass of platinum it should be calcined at an even higher temperature, but the temperature given is sufficient if it is to be used for platinum salts.

Iridium Recovery.—When the solution from the precipitation of platinum with ammonium chloride is left standing, the iridium at length comes down as $(NH_4)_2IrCl_6$. This is filtered, washed, dried, and calcined, giving iridium moss. The iridium moss is then treated with dilute (*i.e.*, 1:3) aqua regia, in which the platinum dissolves and iridium remains insoluble. The platinum solution goes back into the first stage of the process, while the decantate, filtrate, and wash waters from the iridium precipitation are treated with zinc and sulphuric acid, or cast iron and sulphuric acid, throwing down all the heavy metals remaining in solution. This precipitate is known as "first blacks." See also the "lead separation" on page 704.

This is filtered over a vacuum, washed, dried, and put in a bone-ash cupel and roasted in a muffle. A treatment with 1:5 H_2SO_4 will then remove the copper, giving cleaned blacks, which are washed by decantation.

The cleaned blacks are then heated with dilute (1:3) aqua regia, giving Pt, Pd, and traces of Rh and Ir in solution, and Ir and Rh in the residue (insoluble blacks).

Nitrates are removed and the platinum thrown down from solutions as was discussed under Treatment of Platinum Concentrates, on the preceding page. The platinum thus produced is known as "black platinum." The filtrate contains lead, rhodium, and iridium. These are thrown down again with soft iron or zinc and sulphuric acid, the precipitate being known as "second blacks," the second blacks then being roasted and cleaned with HCl (1:3) and redissolved in aqua regia. Evaporate to a spongy consistency with addition of HCl to get rid of the nitric acid compounds, then dissolve the spongy mass in ammonia water. Add hydrochloric acid to acid reaction, and yellow $(NH_4)_2PdCl_6$ should come down. The filtrate carries rhodium and iridium, which should be added to the solution from the insoluble blacks.[2]

[1] Thomas A. Wright says the precipitate will become contaminated with palladium on standing and will be reddish brown and that it should not stand over 5 to 10 min. Further footnotes signed T. A. W. are by Mr. Wright.

[2] To effect the precipitation of platinum with NH_4Cl it is always necessary to remove completely the HNO_3. Otherwise palladium and iridium are precipitated also. Although palladium, when present in appreciable amounts, is precipitated with platinum whether HNO_3 is present or absent, in the last case it is one of occlusion. Palladium forms two salts with NH_4Cl, that of the higher state of oxidation being insoluble in excess of NH_4Cl: that of the lower state of oxidation being soluble.—T. A. W.

Treatment of the Insoluble Blacks.—The insoluble blacks are mixed with three times their weight of BaO_2 and strongly calcined in a coke furnace for 5 or 6 hr. Na_2O_2 may also be used, taking five to ten times as much as there is of the residue. It is best to use fresh Na_2O_2 containing little CO_2.

The mass is ground and dissolved in $15HCl:2HNO_3$, using 4 l. of the mixed acid per kilogram of the mixture of blacks and barium peroxide. The solution should be feebly red.

Evaporate in porcelain to dryness so as to render insoluble the silica which has been introduced by the barium dioxide treatment. Redissolve in hot water, adding a little of the $15HCl:2HNO_3$ mix already used. Settle and decant, and wash the silica residue with hot water.

The consumption of acids can be lessened by leaching the barium dioxide fusion with hot water, discarding the solution, and treating the insoluble residue with the $15HCl:2HNO_3$ mixture.

Precipitate the barium in the solution with H_2SO_4 and filter off the solution. Heat the barium-free solution in porcelain on a sand bath, gradually adding NH_4Cl to saturation. Use about 300 g. of the salt per liter of liquid. After 3 or 4 hr. a purplish black precipitate of $(NH_4)_2IrCl_6$ comes down. Filter and wash until the filtrate is only slightly colored.

The filtrate contains rhodium. It is treated with zinc or iron and sulphuric acid to produce crude rhodium ("rhodium blacks").

Production of Osmium.—Melt the insoluble residues from the original platinum treatment with four or five times their weight of pure zinc, and then heat for several hours at a white heat to distill off the zinc. The fumes from this distillation contain osmium and should not be inhaled.

Powder the residue from this zinc treatment, and mix with three times its weight of BaO_2. Pulverize the "moss" thus obtained. Wash and dry. A train of Wolff bottles is then arranged. The first has three outlets, one used to let in a mixture of 15 parts $HCl:2HNO_3$, as required; the second is used as a steam inlet, and the third connects to the receiving train. In practice, this flask is large enough to contain 10 kg. of moss; 15 l. HCl; 2 l. HNO_3. The moss is placed in the bottle and the train connected, the acid in the above quantity admitted and steam then passed in, the bottle itself being heated. The receiving train consists of five bottles of the same size, in series, the first three containing water, the fourth NaOH, and the fifth Na_2SO_4. Osmium distills; iridium and ruthenium remain behind.

The iridium liquor remaining behind is precipitated hot with ammonium chloride as already described under treatment of the blacks. The ammonium chloriridate is washed, filtered, dried, and calcined to moss, which is cleaned with 1:3 aqua regia. Platinum and palladium that have been carried along this far will dissolve and can be returned to their appropriate place in the cycle.

Take the solution of the osmium in water in porcelain, add NH_4OH to alkalinity, and heat for 1½ hr. Filter, wash, dry, and roast the precipitate to metallic osmium. Look out for the fumes, which are dangerous.

Iridium-ruthenium Separation.—Reduce the ammonium-iridium chloride to "moss." Bring a mixture of 3 parts KOH and 1 part KNO_3 to a quiet fusion and slowly add 1 part of the moss by weight and hold at a dark-red heat for 1½ to 2 hr. Cool and treat the melt with cold water. Na_2O_2 can also be used and some consider it preferable.

K_2RuO_4 dissolves; the iridium is practically insoluble. The ruthenium is then precipitated with zinc.[1]

[1] See *Jour. Am. Chem. Soc.*, December, 1925. Two articles by James Lewis Howe and associates. Separation of ruthenium and solubility of certain of its salts.

Decant and wash the iridium with sodium chlorite until solution is no longer red. Take the insoluble residue and clean it with very dilute hydrochloric acid and calcine. Wash with hot water and very dilute hydrochloric acid. Strong hydrochloric acid carries iridium into solution. Give the insoluble residue a dead roast on the filter.[1]

Take the filtrates and wash waters from all the above treatments and bring everything down as "blacks." Wash and calcine, then dissolve in 1:3 aqua regia.[2] This dissolves the platinum, palladium, and gold[3] and leaves an insoluble residue of rhodium and ruthenium. The gold is precipitated with sulphur dioxide after evaporation with additional hydrochloric acid,[4] and the solution then treated with zinc and sulphuric acid, the precipitate, after calcining and cleaning with HCl, being almost pure palladium, providing the original separations have been carefully made.

Melting of the Platinum Metals.—These metals are all best melted in a crucible made of quicklime, with a cover of the same material. Platinum, like silver, absorbs a relatively large quantity of oxygen when molten. After melting the platinum, this can be burned off by reducing the oxygen blast and allowing an excess of gas to enter the furnace. Palladium is still worse.

Lead Separation of Platinum and Iridium.[5]—The metal is melted with ten times its weight of pure lead in a covered graphite crucible, in which is also placed enough powdered wood charcoal to cover the melt about 1 in.[6] The heating is conducted in a furnace and should be continued at red heat for about 2 hr. After the alloy has cooled, it is removed and the charcoal washed off. The metal is then treated with successive portions of dilute nitric acid (1 to 5) during 4 or 5 hr. (it is well to let it digest overnight). The solution, which contains the lead and some platinum, is separated by decantation through a filter; the residue, containing iridium and platinum, is washed with dilute nitric acid and then with hot water. The filtrate and washings are evaporated until crystals begin to form; then sulphuric acid is added until no further precipitation takes place, a little more being added to be sure of an excess. The white precipitate containing part of the lead as sulphate is removed by filtration and washed with hot water. The filtrate is evaporated on a sand bath until copious white fumes come off; then it is cooled and water is added. The cold solution is filtered, and the white residue containing the rest of the lead is washed with water.

The filtrates and wash waters are evaporated just to dryness and are treated with hydrochloric acid, after which the platinum may be recovered as ammonium chlorplatinate or by precipitation with metallic zinc and hydrochloric acid.

The residue from the nitric acid extraction containing the iridium and the rest of

[1] It is very difficult to wash out the ruthenium salts with sodium hypochlorite and during the operation ruthenium is volatilized and lost. The washing is best done by decantation, as in filtering through paper, the latter becomes clogged by ruthenium reduced by the carbonaceous matter of the filter. The ruthenium is better precipitated with magnesium ribbon, but keep the solution acid or it will be difficult to remove the magnesium salts. Always wash all platinum-group metals precipitated as such with acidified water, and in the case of both finely divided residues and precipitate it is best to use paper pulp in filtering.—T. A. W.

[2] Palladium is soluble with difficulty when oxidized. It should be reduced after calcining.—T. A. W.

[3] It also dissolves some rhodium. Note that when finely divided, freshly precipitated and unignited and undried, these metals are the most readily attacked with acids. When compact or when ignited, iridium, ruthenium, rhodium, and osmium are difficultly soluble. This is the distinction which the literature very often fails to make: therefore the cause for so-called conflicting statements. Of general interest also is the fact that rhodium is found in most all of the aqua regia solutions: ruthenium and osmium rarely.—T. A. W.

[4] Au precipitates thrown down with SO_2 are contaminated with palladium and copper if the latter are present in any quantity.—T. A. W.

[5] From Methods for the Recovery of Platinum, Iridium, etc., from Jewelers' Waste, *U.S. Bur. Mines Tech. Paper* 342.

[6] A porcelain crucible coated with lamp black may be used.—T. A. W.

the platinum is treated for several hours with a mixture of 1 part nitric acid, 4 parts hydrochloric acid, and 9 parts water at a temperature of 80°C. It is well to let this reaction go overnight. The residue is filtered and washed with hot water and is then melted again with lead and treated as before to remove the small quantity of platinum that may still be present.

Osmium Poisoning.—The metal osmium must be handled with great precautions. It oxidizes slowly at room temperatures when finely divided or powdered, and the oxide appears to have a sufficient volatility at ordinary temperatures to make the presence of the powdered metal in the room poisonous to some people. The oxide melts at 40°C. and boils at about 100°C. It is highly irritating to the mucous membranes and to the eyes. While the blindness (or in light poisoning cases, the intense smarting) is usually believed only temporary, and no permanent bad effects are ascribed to osmium fumes, Schoeller and Powell state that the oxide is reduced to metal by contact with the tissue "and the metallic film thus deposited on the cornea produces permanent injury to the eyesight." Osmium fumes should, therefore, be kept as much as possible under a hood, and close-fitting goggles or a gas mask should be worn by anyone exposed to them.

OsO_4 reacts with hydrochloric acid of 1.16 sp. gr., but not with weaker solutions, forming $OsCl_4$.

Ruthenium.—R. A. Cooper[1] says that ruthenium fumes, like those of osmium, are hard on the eyes of anyone working with them. The RuO_4 begins to volatilize at about 600°C.

A concentrated solution of RuO_4 will dissolve with concentrated NH_4OH to form gray-brown $(NH_4)_2RuO_5$. RuO_4 reacts with HCl of over 1.160 density to form $RuCl_4$, but does not react with acid below that strength.

It should be noted that the methods here given for the treatment of the platinum metals are essentially the same as presented by Louis du Parc in "Le Platine du Mende," referred to in Chap. XI.

[1] *Jour. Chem. Met. Soc. S. Africa*, Vol. 22, p. 152, 1932.

APPENDIX

METRIC-ENGLISH EQUIVALENTS

Length

1 ft. = 0.30480060096 m.
1 in. = 2.540005 cm.
1 m. = 3.28083 ft. = 39.370000 in.

Area

1 sq. in. = 6.452 sq. cm.
1 sq. ft. = 0.09290 sq. m.
1 sq. yd. = 0.83613 sq. m.
1 sq. m. = 1.1960 sq. yd. = 10.764 sq. ft.
1 sq. cm. = 0.15500 sq. in.

Volume

1 cu. yd. = 0.764559445 cu. m.
1 cu. ft. = 0.028317 cu. m.
1 cu. in. = 16.3872 cc.
1 cu. ft. = 28.316 l.
1 cu. in. = 16.3867 ml.
1 cu. m. = 1.3079 cu. yd.
1 cc. = 0.06102 cu. in.
1 l. = 61.025 cu. in. = 0.035315 cu. ft.

Mass

1 lb. (avoirdupois) = 0.4535924277 kg.
1 oz. (avoirdupois) = 28.3495 g.
1 oz. (troy) = 31.10348 g.
1 dram (ʒ = 3 ℈, apoth.) = 3.887935 g.
1 kg. = 2.20462234 lb. (avoirdupois) = 2.67923 lb. (troy)
1 g. = 0.035274 oz. (avoirdupois) = 0.032151 oz. (troy) = 15.4324 grains

Capacity

1 qt. (liquid) = 0.94633307 l.
1 qt. (dry) = 1.1012 l.
1 l. = 1.05671 qt. (liquid) = 0.9081 qt. (dry) = 33.8147 fl. oz.
1 fl. oz. = 0.0295729 l. = 1.80469 cu. in.

NOTE.—1 gal. (liquid) = 231.0 cu. in.
1 bu. (dry) = 2,150.42 cu. in.
1 l. = 1,000.027 cc.

Energy

1 hp. = 0.746 kw. = 33,000 ft.-lb. per min.
1 kw. = 1.341 hp. = 1,000 joules per sec.
1 ft.-lb. = 1.383 $\times$ 10^7 ergs = 1.383 joules = 0.1383 kg.-m.
1 poundal = 13,825 dynes.
1 gram's weight = 980 dynes.
1 pound's weight = 444,518 dynes.
1 hp.-year = 6,535 kw.-hr.
1 kw.-yr. = 11,747 hp.-hr.

INTERNATIONAL ATOMIC WEIGHTS, 1943

Element	Symbol and atomic number	Weight	Valence[1]	Electrochem. equivalents, g. per amp.-hr.	Melting points, deg. C.	Boiling points, deg. C., visible ebullition
Aluminum	Al(13)	26.97	3	0.3355	658.7	1800.0
Antimony	Sb(51)	121.76	3	1.5145	630.0	1460.0
Argon	A(18)	39.9	0	......	−189.3	−186.0
Arsenic	As(33)	74 91	3	0.9318	850.0	450.0[2]
Barium	Ba(56)	137.36	2	2.5619	850.0	
Beryllium	Be(4)	9.02	2	0.1683	1285.0	
Bismuth	Bi(83)	209.0	3	2.5992	271.0	1440.0
Boron	B(5)	10.82	3	......	2350.0	3500[2]
Bromine	Br(35)	79.92	1	2.9814	−7.3	58.75
Cadmium	Cd(48)	112.41	2	2.0974	320.9	778.0
Caesium	Cs(55)	132 91	1	......	26.0	
Calcium	Ca(20)	40.08	2	0 7478	810 0	
Carbon	C(6)	12.01	4	0.1118	>3600.0	3700.0
Cerium	Ce(58)	140 13	3	1 7426	623.0	
Chlorine	Cl(17)	35.46	1	1.3230	−101.5	−37.6
Chromium	Cr(24)	52.01	3	0.6470	1520 to >Fe	2200.0
Cobalt	Co(27)	58.94	3	1.1000	1610[3]	
Columbium	Cb(41)	92.91	5	......	1950–2200	
Copper	Cu(29)	63.57	2	1.1858	1083.0	2100.0
Dysprosium	Dy(66)	162.46	3			
Erbium	Er(68)	167 2	3			
Europium	Eu(63)	152 0	3			
Fluorine	F(9)	19.0	1	0.7085	−223.0	−187.0
Gadolinium	Gd(54)	156 9	3			
Gallium	Ga(31)	69.72	3	......	30.1	
Germanium	Ge(32)	72.6	4	......	958.0	
Gold	Au(79)	197 2	3	2.4522	1063.0	2100.0
Hafnium	Hf(72)	178.6				
Helium	He(2)	4.003	0	......	−271.9	−268.8
Helvetium	Hv(85)					
Holmium	Ho(67)	164.94				
Hydrogen	H(1)	1.008	1	0.03761	−259.0	−252.8
Illinium	Il(61)					
Indium	In(49)	114.76	3	1.4271	154.5	1000.0
Iodine	I(53)	126.92	1	4.7353	114.0	184.35
Iridium	Ir(77)	193.1	4	......	2300.0	2850.0
Iron	Fe(26)	55.85	2	1.0416	1530 ± 5	2450.0
Krypton	Kr(36)	83.70	0	......	−169.0	−151.7
Lanthanum	La(57)	138.92	3	......	810.0	
Lead	Pb(82)	207.21	2	3.8651	327.4	1525.0
Lithium	Li(3)	6.94	1	0.2589	186.0	500.0
Lutecium	Lu(71)	174 99	3			
Magnesium	Mg(12)	24.32	2	0.4536	651.0	1120.0
Manganese	Mn(25)	54.93	2	1.0255	1260 ± 20	1900.0
Masurium	Ma(43)					
Mercury	Hg(80)	200.61	2	7.4840	−38.87	357.0
Molybdenum	Mo(42)	95.95	2	1.7903	2550.0	3350.0
Neodynium	Nd(60)	144.27	3	......	840.0	
Neon	Ne(10)	20.18	0	......	−253.0	−245.9

[1] In those cases in which a metal has two valences, the valence given corresponds to the electrochemical equivalent, and may not necessarily be the commoner one.
[2] Sublimes. [3] Commercial metal, about 1480°C.

INTERNATIONAL ATOMIC WEIGHTS, 1943.—(*Continued*)

Element	Symbol and atomic member	Weight	Valence[1]	Electro-chem. equivalents, g. per amp.-hr.	Melting points, deg. C.	Boiling points, deg. C., visible ebullition
Nickel	Ni(28)	58 69	2	1.0951	1452 ± 3	2450.0
Nitrogen	N(7)	14.008	3	0.1742	−210.5	−195.7
Osmium	Os(76)	190.2	4	.....	2700.0	2950.0
Oxygen	O(8)	16.00	2	0 2985	−218.0	−183.0
Palladium	Pd(46)	106.7	2	1.9903	1550.0	2540.0
Phosphorus	P(15)	30.98	..	......	44.1	287.0
Platinum	Pt(78)	195 23	4	1.8206	1755.0	2650.0
Polonium	Po(84)	214.2	4	1.9586		
Potassium	K(19)	39.096	1	1.4590	62.3	667.0
Praseodymium	Pr(59)	140 92	3	......	940.0	
Protactinium	Pa(91)	231	5			
Radium	Ra(88)	226.05	2	......	900.0	
Radon	Rd(86)	222.4	0	......	−71.0	−62.0
Rhenium	Re(75)	186 31	4			
Rhodium	Rh(45)	102 91	3	1.2797	1940.0	2750.0
Rubidium	Rb(37)	85.48	1	......	38.0	696.0
Ruthenium	Ru(44)	101 7	4	......	>1950.0	2780.0
Samarium	Sa(62)	150.43	3	......	1350 0	
Scandium	Sc(21)	45.10	3	.....	1200.0(?)	
Selenium	Se(34)	78.96	2	1.4733	218.5	690.0
Silicon	Si(14)	28.06	4	0 2618	1420 0	3800.0
Silver	Ag(47)	107.88	1	4.0245	961.0	1955.0
Sodium	Na(11)	22.997	1	0.8579	97.5	742.0
Strontium	Sr(38)	87.63	2	1.6333	>Ca <Ba	
Sulphur	S(16)	32.06	2	0.5980	122.8–119.2	444.5
Tantalum	Ta(73)	180.88	5	......	2850.0	
Tellurium	Te(52)	127.01	2	2.3803	451.0	1390.0
Terbium	Tb(65)	159.2	3			
Thallium	Tl(81)	204.39	1	7.6249	302 0	1700.0[2]
Thorium	Th(90)	232.12	4	2.1649	>1700.0 <Pt	
Thulium	Tm(69)	169.4	3			
Tin	Sn(50)	118.7	2	2.2141	231.9	2270.0
Titanium	Ti(22)	47.9	4	0.4490	1795.0 ± 150.	2700.0
Tungsten	W(74)	183.92	6	1.1493	3267 0	3700.0
Uranium	U(92)	238.07	4	......	Near Mo.	3100.0
Vanadium	V(23)	50 95	5	......	1720.0 ± 20.0	
Xenon	Xe(54)	131.3	0	......	−140 0	−109.1
Ytterbium	Yb(70)	173.04	3	......	1800.0(?)	
Yttrium	Yt(39)	88 92	3	......	1490.0	
Zinc	Zn(30)	65.30	2	1.2199	419.4	918.0
Zirconium	Zr(40)	91.22	4	......	1700.0(?)	

NOTE.—The hypothetical coronium, supposed to exist in the solar corona, has lately been shown to be highly ionized nickel, calcium, and iron.

[1] In those cases in which a metal has two valences, the valence given corresponds to the electrochemical equivalent, and may not necessarily be the commoner one.

[2] Also given as 1280°C.

The Atomic Numbers

(The arrangement is like that of a logarithmic table. The first figure of the number is given by column 1, the second figure by the numbers at the tops of the columns.)

	0	1	2	3	4	5	6	7	8	9
0	..	H	He	Li	Be	B	C	N	O	F
1	Ne	Na	Mg	Al	Si	P	S	Cl	A	K
2	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
3	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y
4	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In
5	Sn	Sb	Te	I	Xe	Cs	Ba	La	Ce	Pr
6	Nd	[1]	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm
7	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au
8	Hg	Tl	Pb	Bi	Po(?)	[2]	Rd	[3]	Ra	Ac(?)
9	Th	Pa	U							

[1] Named illinium by the discoverers, B. S. Hopkins, J. A. Harris, and L. F. Yntema. Probably Rolla's florentium.

[2] Possibly helvetium—Dr. Walther Minder.

[3] Possibly virginium—Dr. F. Allison.

Equilibrium Conditions for Sulphates

$Fe_2(SO_4)_3 \rightleftarrows Fe_2O_3 + 3SO_3$		$Al_2(SO_4)_3 \rightleftarrows Al_2O_3 + 3SO_3$		$2CuSO_4 \rightleftarrows 2CuO.SO_3 + SO_3$		$2CuO.SO_3 \rightleftarrows 2CuO + SO_3$		$ZnSO_4 \rightleftarrows ZnO + SO_3$	
Temperature	Millimeters	Temperature	Millimeters	Temperature	Millimeters	Temperature	Millimeters	Temperature	Millimeters
553°	23	572°	28	546°	43	600°	62	675°	5
570°	33	621°	51	588°	55	653°	98	690°	6
592°	45	681°	120	615°	70	686°	123	720°	24
614°	70	702°	180	642°	98	705°	139	750°	61
634°	113	720°	261	665°	130	728°	173	775°	112
650°	149	731°	356	700°	233	745°	209	800°	189
660°	182	742°	480	714°	324	775°	298		
680°	286	748°	692	725°	460	805°	542		
690°	401	...	...	731°	647				
699°	560								
707°	715								

Temperature in degrees centigrade.

INDEX

The subject matter of the other volume is not indexed here

The subject matter of the other volume is not indexed here

The subject matter of the other volume is not indexed here

The subject matter of the other volume is not indexed here

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